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THEORETICAL STUDY OF ATOMIC AND MOLECULAR PROCESSES

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GCA CORPORATION

Bedford, Massachusetts

FINAL REPORT

Contract No. DASA01-70-C-0091

Prepared for

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ABSTRACT

This report presents the findings of a number of individual investigations relevant to the physics of atomic and molecular processes in the upper atmosphere as pertinent to the problem of the rate of reduction of ionization in a disturbed atmosphere.

Calculations have been performed of the rates for three-body ion-electron recombination

$$X^+ + e + M \rightarrow X + M$$

for a variety of ions X^+ and third bodies M. Emphasis has been placed on systems where the third body involves a molecular species. It has been shown that if the third body has low energy modes of internal excitation, large recombination rates may result. If M is a polar molecule, very large recombination rates will result. The calculations show that the rate for three-body ion-electron recombination is very sensitive to the concentration of water vapor.

The process of associative detachment

$$X^- + Y \rightarrow XY + e$$

is an important mechanism for the removal of negative atomic and molecular ions. Only sparse accurate experimental data exist, and quantitative theoretical data exist only for H^- + H collisions. Quantitative prediction of the rate coefficient for associative detachment requires accurate potential energy curves for the negative molecular ion XY^- and the neutral molecule XY, especially in any regions of curve crossings involving the lower levels of the molecules. Also required are certain non-radiative coupling matrix elements between the electronic states of the molecules. The theoretical calculation of the necessary accurate potential energy curves and matrix elements represents a relatively

difficult theoretical problem for species of interest in the atmosphere. From knowledge of the potential energy curves, useful upper limits for the rate of associative detachment can be obtained. Improved calculations of potential energy curves O_2^-, relative to theoretical O_2 curves, have been performed for the important atmospheric process

$$O^- + O \rightarrow O_2 + e$$

the cross section could be as large as $4.6\ \pi a_o^2$.

The cross section for rotational excitation in electron polar molecule collisions,

$$e + M(J) \rightarrow e + M\ (J + \Delta J),$$

where M(J) is a polar molecule in rotational state J, is large. Rotational excitation processes represent an important energy loss mechanism for the thermalization of supra-thermal electrons produced by an atmospheric disturbance. Since most recombination processes proceed much more rapidly for low energy electrons than for supra-thermal electrons, the rotational excitation process plays an important role in the rate of reduction of ionization in a disturbed atmosphere. The cross section for this process constitutes an essential input data point for the studies of three-body ion-electron recombination in polar gases. Detailed calculations have been performed for the cross section for rotational excitation of carbon monoxide by electron impact using close-coupling methods.

FOREWORD

This report was prepared by GCA Corporation, Bedford, Massachusetts under Contract No. DASA01-70-C-0091. The research was performed under NWER Subtask HD028. Professors D. R. Bates and J. C. Browne made considerable contributions to the research program.

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I. INTRODUCTION

A detailed understanding of the behavior of the atmosphere following a severe disturbance requires detailed knowledge of cross sections and rate coefficients for a highly diverse ensemble of atomic, molecular, and chemical processes involving ambient atmospheric species. Under DNA sponsorship for the past several years, GCA Technology Division has been engaged in theoretical studies of various selected atomic and molecular processes which are relevant to the understanding of a disturbed atmosphere. Most of the processes which have been studied pertain to the problem of the rate of reduction of ionization following a severe disturbance since this constitutes an important operational factor of interest to the sponsoring agency. Three major criteria were employed in the selection of processes for detailed investigation, as characterized by the following specific questions:

(1) What is the over-all importance or potential importance of the process in the understanding of the de-ionization of the disturbed atmosphere: (In certain instances the pertinent rate coefficients were sufficiently uncertain as to require preliminary investigation simply to assess their relative importance.)

(2) Can quantitative theoretical calculations be performed to useful accuracy for atmospheric species?

(3) Are theoretical studies required either to assess the accuracy or in other useful ways to supplement available experimental data?

Several processes were evaluated briefly and were found not to satisfy one or more of the above criteria and consequently were removed from further consideration. Of the remaining candidates, four specific processes were selected for further detailed investigation as reported herein. Although each process is believed to have relevance to the general ambient ionization reduction problem in conformity with item (1) above, they are sufficiently independent to warrant individual attention. Specifically the de-ionization mechanisms considered include: (1) three-body recombination, (2) ion-ion neutralization and (3) associative detach-

ment. Finally some attention has been given to the theoretical problem of using effective potentials to calculate molecular wave functions and potential energy curves for diatomic molecules. These studies may then be related to pertinent atmospheric change transfer and scattering processes. As a consequence, the detailed results of these investigations are presented in Sections II through V of this report as discussed below.

In Section II, three body ion-electron recombination processes such as

$$X^+ + e + M \rightarrow X + M$$

are discussed. This represents an important processes in the D-region at its relatively low temperature and high neutral particle density, especially for those ions which do not undergo exothermic chemical reactions. Preliminary calculations were performed for various ions in atomic third body species, where proper account was taken of the velocity dependence of the electron third body scattering cross section (Ref. I-1). Since most atomic species have no low energy modes of internal excitation, only elastic electron third body scattering contributes and the resultant recombination coefficient is not very large, although it can exceed pure radiative recombination. Atomic oxygen represents an exception, since fine structure transitions in the ground state occur at low energies. However, in the D-region the atomic oxygen concentration is not large and molecules should constitute the major class of third bodies.

Calculations have been performed previously for several homonuclear third bodies (Ref. I-2). Because of low energy rotational and vibrational modes of internal excitation, the recombination rate coefficients for molecular third bodies were found to be much larger than those obtained for atomic third body systems. The present calculations were performed for polar molecule third body systems. Owing to the relatively long range nature of the electron-permanent dipole interaction, the cross section for rotational excitation of polar molecules is very large, so that correspondingly high three body ion electron recombination coefficients result. The inelastic cross section for these systems exceeds the elastic cross section.

These calculations demonstrate that, since three body ion-electron recombination coefficients involving polar molecule third bodies are often several orders of magnitude faster than coefficients for atomic species, the over-all recombination rate in dense neutral gases is a sensitive function of the polar molecule concentration. The theoretical studies conducted to date has provided sufficient information to estimate the recombination coefficient for an extensive class of ions in various gases under a broad range of conditions. The detailed application to disturbed atmospheres requires quantitative data on competing ion-electron recombination processes, as well as the pertinent rates for attachment, detachment, and ionizing processes under the atmospheric conditions of interest. The results of the present study assume added importance in the study of disturbed atmospheres since the concentration of polar molecules may be enhanced significantly by chemical and ion-molecule reactions under disturbed conditions.

In studies of recombination following an atmospheric disturbance, it has become clear that atomic and molecular processes which thermalize the original supra-thermal electrons are important, especially in a nearly neutral atmosphere. Elastic electron-atom and electron-molecule processes are very inefficient for the critical energy region, and inelastic events due to electronic excitation are improbable. Rotational excitation of polar molecules represents an efficient energy loss mechanism resulting in the thermalization of supra-thermal electrons, due to the very long-range electron-polar molecule interactor (which leads to large inelastic scattering cross sections). Since the effective rates for recombination and attachment are much larger for thermal as opposed to supra-thermal electrons, the rate of thermalization of supra-thermal electrons may represent the controlling processes in recombination following a severe atmospheric disturbance, especially since the disturbed atmosphere may have an enhanced concentration of polar molecules.

Detailed calculations have been performed to derive the cross section for rotational excitation of CO and CN by electron impact in Sec-

tion III. Angular distributions and momentum transfer cross sections have been obtained. Since the elastic scattering cross section at these energies is small compared to the inelastic cross section, the full implementation of a close-coupling formalism is required. By studying the process in various polar molecules, it is possible to determine the dependence of the resultant cross sections on such parameters as the dipole moment and rotational energy separation of the polar molecules. Calculations should also be performed for water vapor and other polar molecules of atmospheric interest; however, the results presently available indicate that the process is important for the understanding of the behavior of the disturbed atmosphere. The cross sections are also of importance for the calculation of three-body ion-electron recombination in polar gases as discussed above.

In studies of a low temperature, high neutral density atmosphere under either normal or disturbed conditions, significant concentrations of negative ion species exist. Ion-molecule reactions and chemistry often are seen to lead to those negative ions with the largest electron affinity. Investigations of the loss rates of negative ions are required for the satisfactory prediction of the rate of decrease of atmospheric ionization. Under the thermodynamic conditions usually encountered, direct collisional detachment has a very small rate coefficient because of the endothermicity requirements imposed by the relevant electron affinities.

Under a previous program (Ref. I-3), a study has been performed of the mutual neutralization process

$$X^+ + Y^- \rightarrow X + Y$$

which represents one of the most important mechanisms for the destruction of negative ions in the atmosphere. Although serious discrepancies exist between the theoretical results and available experimental data, which will not be discussed here, all studies show that a very large rate coefficient exists for the mutual neutralization process at thermal energies.

In an essentially neutral atmosphere, such as that encountered in the D-region, the associative detachment process

$$X^- + Y \rightarrow XY + e$$

may be as important, or even more important than the mutual neutralization processes for the destruction of negative ions as discussed in Section IV in greater detail. For atmospheric species, the prediction of the pertinent associative detachment cross sections constitutes a relatively severe theoretical and experimental problem. Quantitative calculations have been performed only for the simple prototype system $H + H^-$. The temperature dependence of the process is still somewhat uncertain, and quantitative predictions require very accurate potential energy curves and coupling matrix elements. In order to study the process, improved accurate potential energy curves have been calculated for the O_2^- ($^2\Pi_g$) state relative to the $O_2(X\ ^3\Sigma_g^-)$ curve of Schaefer-Harris (Ref. I-4). Certain errors detected in the Schaefer-Harris calculations have required a recalculation of our O_2^- curves. From these data, accurate values for the internuclear separation associated with the crossing of the $O_2^-(^2\Pi_g)$ and $O_2(X\ ^3\Sigma_g^-)$ curves can be achieved and an upper limit for the rate of reaction for the important atmospheric associative detachment process

$$O^- + O \rightarrow O_2 + e$$

can be obtained. Although the accurate ab-initio calculation of potential energy curves for associative detachment processes in atmospheric species is relatively expensive and slow, the results of such studies are required in order to understand the process, especially since the required non-radiative coupling matrix elements can seldom be determined by other methods. The necessary data on the required potential energy curves cannot usually be obtained by the Rydberg-Klein-Rees analysis of experimental spectroscopic data.

Under the current program, a new area of investigation was pursued involving exploration of the possibility of using effective potential

methods to calculate molecular wavefunctions and potential energy curves for diatomic molecules at intermediate internuclear separations as discussed in Section V. Encouraging results were obtained for the simple system chosen for the initial investigation, Li_2^+. However, although these preliminary calculations were very successful, it is considered that current technical limitations inherent in the methods preclude the derivation of accurate data at the present time for most systems of atmospheric interest without resort to an extensive and moderately expensive research program.

As indicated above, the four processes which were selected for detailed investigation under the present program are discussed individually in the following sections of the report. Individual contributing investigators are identified in each section. A brief conclusion and recommendations for future study discussion is presented in Section VI.

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II. ELECTRON-ION RECOMBINATION IN A DENSE MOLECULAR GAS

by D. R. Bates

ABSTRACT

A semi-quantal method is developed for treating the recombination of electrons and positive ions in a dense molecular gas. Extensive calculations are carried out relating to recombination in hydrogen, in nitrogen, in carbon dioxide and in damp mixtures of gases. This latter case is of special interest, recombination being greatly facilitated by the presence of quite a small amount of water vapor. A very high recombination coefficient is possible. For example in a nitrogen + hydrogen mixture which contains 20% by volume of water vapor and which is at atmospheric pressure and at 2000 K the recombination coefficient is predicted to be between about 5.1×10^{-9} cm^3 s^{-1} and 8.7×10^{-9} cm^3 s^{-1}: here the lower limit is calculated by the semi-quantal method assuming that the energy levels of the recombining system are hydrogenic while the upper limit is calculated by a purely classical method assuming that the energy levels of the recombining system form a continuum.

Recombination coefficients have been deduced from measurements on the ionization in flames at atmospheric pressure. The values obtained lie satisfactorily between the predicted limits.

A. INTRODUCTION

Three-body ion-electron recombination processes

$$X^+ + E + M \rightarrow X + M$$

may be an important recombination process in the D region at its lower temperatures and higher densities, especially for those ions which do not undergo chemical reactions. In earlier studies it was shown that much higher recombination coefficients were obtained if the third body M in the above equation exhibits low energy degrees of internal freedom as is the case for a large class of molecular third bodies. In the

present report, attention has been focused on the polar molecule H_2O as the third body. Calculations have been carried out for recombination in several reactions of diatomic third bodies with water vapor. The results have been obtained at several temperatures and mixing ratios. For an ion of mass 23 a.m.u., a recombination coefficient of the order of 10^{-5} cm^3 sec^{-1} can be obtained for ~ 20% by volume mixtures of H_2O in N_2 at 250°K, where the recombination coefficient is expressed as an effective two-body coefficient.

B. BACKGROUND

Recombination of electrons and ions in a dense neutral gas was first treated by Thomson (1924) using a modification of his model for three-body ion-ion recombination (Massey and Burhop 1952). An entirely different approach was introduced by Pitaevskii (1962). Taking the neutral gas to be monatomic he showed that if the temperature is sufficiently low the recombination process may be regarded as classical diffusion in energy space; and from the Fokker-Planck equation he hence derived a simple formula for the recombination coefficient. Pitaevskii's classical diffusion method was later applied to a molecular gas by Dalidchik and Sayasov (1966, 1967). Its main defects are the assumption that the negative energy levels of the electron in the field of the ion form a continuum, and the lack of explicit allowance for radiative transitions. Bates and Khare (1965) have developed a semi-quantal method without these defects. However, they confined their attention to the case of a monatomic gas where all collisions are elastic. Their results agree with those of Pitaevskii only at very low temperatures. It is of interest to extend the method to cover recombination in a molecular gas. Inelastic collisions, involving rotational or vibrational transitions, are here important.

The process with which we shall be concerned is of importance in connection with ionization in flames.

C. THEORY

We shall treat

$$X^+ + e + Z \rightarrow X + Z \qquad \text{(II-1)}$$

where X^+ is an atomic or molecular ion and where Z is a neutral molecule. In this section we shall introduce the notation and quote the relevant formulae of the semi-quantal method.

Averaging over the initial rotational and vibrational levels of Z, which we suppose to be in thermodynamic equilibrium at temperature θ, and summing over all possible final levels, let $\kappa(n,m)$ be the rate coefficient for

$$X(n) + Z(\text{averaged}) \rightarrow X(m) + Z(\text{summed}) \qquad \text{(II-2)}$$

n and m being the principal quantum numbers of excited (and assumed by hydrogenic) initial and final states of the system formed by recombination. Put

$$\epsilon(n) = e^2/2n^2a_0 k\theta, \qquad \text{(II-3)}$$

where a_0 is the atomic unit of length. Write

$$\mathscr{G}(q) = N(Z)\sum_{s=0}^{\infty}\sum_{t=0}^{q-q_0-1}(1+s+t)(q+s)^2\kappa(q+s,q-1-t)\exp[\epsilon(q+s)], \qquad \text{(II-4)}$$

where N(Z) is the number density indicated and q_0 is the principal quantum number of the highest level whose population may rise sufficiently to deplete the population of the continuum appreciably (which number may in practice be taken to be 3 without causing appreciable error); write

$$\mathscr{A}(q) = q^2A(q)\exp[\epsilon(q)],$$

where A(q) is the sum of the spontaneous transition probabilities from level q to all lower levels except the ground level (which is excluded because of self-absorption); and write

$$\mu(q) = \frac{\mathscr{G}(q+1)}{\mathscr{G}(q+1)+\mathscr{A}(q+1)}.$$

Let α_R be the radiative recombination coefficient. From the work of Bates and Khare (1965) we have that the rate coefficient describing recombination due to the combined effect of collisions and radiative transitions is closely

$$\alpha_{CR} = \alpha'_{CR} + \alpha_R, \tag{II-5}$$

in which

$$\alpha'_{CR} = V\left\{\sum_{q=q_c+1}^{\infty} \frac{\mu(q)}{\mathscr{C}(q)+\mathscr{A}(q)}\right\}^{-1}, \tag{II-6}$$

with

$$V = \left(\frac{h^2}{2\pi m_e k\theta}\right)^{\frac{3}{2}} = 1.31\times 10^{-20}\left(\frac{1000}{\theta}\right)^{\frac{3}{2}} \text{cm}^3. \tag{II-7}$$

The atomic mass of the ion and the chemical symbol for a molecule of the ambient gas will be shown in brackets after α_{CR} where this is judged desirable.

Dissociative recombination also occurs if the ions are molecular. The rate coefficients are approximately additive.

The transition probabilities required for the radiative conductances $\mathscr{A}(q)$ are known (see Refs. cited by Bates and Khare (1965), and also Wiese, Smith and Glennon (1966) and Wiese, Smith and Miles (1969)). Table II-1 gives the values of $\mathscr{A}(q)$ for atomic hydrogen, which we denote by $\mathscr{A}(q|H)$ together with the factors f(n) by which these radiative conductances would be reduced if transitions to level n or lower were excluded. The information contained enables estimates for complex atoms, which are accurate enough for present purposes, to be made quickly.

TABLE II-1. RADIATIVE CONDUCTANCES

	temperature, θ/K					
	250	500	1000	2000		
	$\mathscr{G}(q\|H)/s^{-1}$					
q					$f(2)$	$f(3)$
3	1.2^{20}	6.0^{18}	1.7^{16}	2.6^{15}	0	—
4	3.9^{16}	1.7^{17}	5.4^{15}	3.9^{15}	0.52	0
5	1.7^{19}	5.7^{8}	1.0^{11}	4.4^{9}	0.66	0.36
6	5.3^{15}	8.2^{11}	1.0^{10}	1.1^{9}	0.73	0.50
7	3.6^{13}	5.7^{1}	2.3^{9}	4.6^{8}	0.76	0.58
8	1.3^{13}	9.3^{9}	7.9^{8}	2.3^{8}	0.79	0.63

The indices give the powers of 10 by which the entries should be multiplied.

The calculation of the binary rate coefficients, $\kappa(n,m)$, and hence of the collisional conductances, $\mathscr{G}(q)$, is the main task.

1. Rate Coefficient $\kappa(n,m)$

Consider collisions between free electrons and molecules which are in a specified level. Let $K_I(E_1,E_2)dE_2$ be the rate coefficient for collisions in which the energy of an electron is changed from E_1 to between E_2 and $E_2 + dE_2$ and the internal energy of a molecule is increased by an amount I.

Denote the masses of the ion and electron by M_X and m_e respectively. Take V_{e1} and V_{e2} to be the velocities of the electron relative to the ion before and after the collision; and take V_{Z1} and V_{Z2} to be the corresponding velocities of the molecule. Write

$$U = V_{Z1} - \frac{m_e}{m_e + M_X} V_{e1}. \tag{II-8}$$

We find that to a close approximation

$$E_2 - E_1 = -I - J - \delta, \tag{II-9}$$

where

$$J = m_e U.(V_{e1} - V_{e2}) \tag{II-10}$$

and

$$\delta = (m_e^2/M_{XZ})\, V_{e1} \cdot (V_{e1} - V_{e2}), \qquad \text{(II-11)}$$

M_{XZ} being the reduced mass of the ion and molecule.

In the first instance we shall suppose that δ, which is in general very small compared with I + J, may be neglected. We shall assume that

$$\frac{m_e}{M_X} V_{e1} \ll U. \qquad \text{(II-12)}$$

For simplicity we shall also assume that the e–Z scattering is isotropic so that the orientations of V_{e1} and V_{e2} with respect to U are random. In many cases the scattering is non-isotropic (Bardsley and Reed 1968) but the error arising is unlikely to be serious.

Represent the scattering cross-section and the normalized classical distribution functions (Bates and Khare 1965) by $\sigma_I(V_{e1})$, $g(V_{e1})$ and f(U) respectively. Put

$$\mu_1 = \hat{U} \cdot \hat{V}_{e1}, \quad \mu_2 = \hat{U} \cdot \hat{V}_{e2}. \qquad \text{(II-13)}$$

We then have that

$$K_I(E_1, E_2)\, dE_2 = \frac{1}{4} \int\int\int_{\mathcal{S}} V_{e1}\, \sigma_I(V_{e1})\, g(V_{e1})\, f(U)\, d\mu_1\, d\mu_2\, dU\, dV_{e1}, \qquad \text{(II-14)}$$

where $\mathcal{S}$ signifies that the integration is carried out over all accessible regions in which the final kinetic energy of the electron is within an interval dE_2 around the value E_2. The lowest contributing value of V_{e1} is

$$\left.\begin{aligned} V_0 &= (2I/m_e)^{\frac{1}{2}} \quad (I > 0) \\ &= 0 \qquad\qquad (I < 0), \end{aligned}\right\} \qquad \text{(II-15)}$$

and the highest is a cut-off value V_c defined by

$$\tfrac{1}{2}m_e V_0^2 = E_1 + e^2/r_0, \tag{II-16}$$

r_0 being the closest the electron can be to the ion and yet be considered as colliding with the molecule. For a given value of V_{e1}, it is clear that

$$U_c < U < \infty, \tag{II-17}$$

where

$$U_c = |J|/m_e[V_{e1} + (V_{e1}^2 - 2I/m_e)^{\frac{1}{2}}]. \tag{II-18}$$

It is now convenient to denote the greater of V_{e1} and V_{e2} by V> and the lesser by V< and to put

$$\mu_> \equiv \hat{V}_> \cdot \hat{U}, \quad \mu_< \equiv \hat{V}_< \cdot \hat{U}. \tag{II-19}$$

If J, U, V> and V< are held fixed while $\mu_<$ is varied the extent of the range $\mu_>$ is

$$\left.\begin{aligned} \mathcal{A} &= 2V_</V_>, \quad 0 \leqslant |J| \leqslant m_e U(V_> - V_<) \\ &= \frac{m_e U(V_> + V_<) - |J|}{m_e U V_>}, \quad m_e U(V_> - V_<) \leqslant |J| \leqslant m_e U(V_> + V_<). \end{aligned}\right\} \tag{II-20}$$

We find that

$$K_I(E_1, E_2) = \int_{V_c}^{V_\infty} V_{e1}\, \sigma_I(V_{e1})\, g(V_{e1})\, \mathcal{J}(V_{e1})\, dV_{e1} \tag{II-21}$$

with

$$\mathcal{J}(V_{e1}) = \frac{1}{4m_e V_<} \int_{U_c}^{\infty} \mathcal{A}\, U^{-1} f(U)\, dU. \tag{II-22}$$

Set

$$-E_1/k\theta \equiv \lambda_1, \quad -E_2/k\theta \equiv \lambda_2, \tag{II-23}$$

$$I/k\theta \equiv \nu, \quad J/k\theta \equiv \eta. \tag{II-24}$$

$$m_e V_{e1}^2/2k\theta \equiv x, \quad (e^2/k\theta r_0) - \lambda_1 \equiv x_c, \tag{II-25}$$

$$\sigma_I(V_0) \equiv \sigma_\nu(x), \tag{II-26}$$

$$\eta^2/4\{x^{\frac{1}{2}} - (x-\nu)^{\frac{1}{2}}\}^2 \equiv X^-, \quad \eta^2/4\{x^{\frac{1}{2}} + (x-\nu)^{\frac{1}{2}}\}^2 \equiv X^+, \tag{II-27}$$

$$2M_{XZ}/m_e \equiv l \tag{II-28}$$

and

$$K_I(E_1, E_2)\,dE_2 \equiv \kappa_\nu(\lambda_1, \lambda_2)\,d\lambda_2. \tag{II-29}$$

By straightforward analysis we deduce from (II-21) that

$$\kappa_\nu(\lambda_1, \lambda_2) = 4\left\{\frac{lk\theta\lambda_1^5}{m_e\pi^3}\right\}^{\frac{1}{2}} \mathcal{J}_\nu, \tag{II-30}$$

where

$$\mathcal{J}_\nu = \int_{x_0}^{x_c} \frac{\sigma_\nu(x)}{(x+\lambda_1)^4}\,\mathcal{K}(x)\,dx,$$

$$\mathcal{K}(x) = (k_1+k_2)\exp[-\tfrac{1}{2}lX^+] - (k_1-k_2)\exp[-\tfrac{1}{2}lX^-] \tag{II-31}$$

$$+ |\eta|\left\{\frac{l\pi x}{8(x-\nu)}\right\}^{\frac{1}{2}}\{\mathrm{erf}[\tfrac{1}{2}lX^+]^{\frac{1}{2}} - \mathrm{erf}[\tfrac{1}{2}lX^-]^{\frac{1}{2}}\}, \tag{II-32}$$

in which

$$x_0 \equiv \nu, \quad k_1 \equiv x/(x-\nu)^{\frac{1}{2}}, \quad k_2 \equiv x^{\frac{1}{2}}, \tag{II-33}$$

if ν is positive; and in which

$$x_0 \equiv 0, \quad k_1 \equiv x^{\frac{1}{2}}, \quad k_2 \equiv x^{\frac{1}{2}}/(x-\nu)^{\frac{1}{2}}, \tag{II-34}$$

if ν is negative.

As a partial check it may be noted that if we take x_c to be infinite we may deduce from (II-30) that the rate coefficient describing the excitation of the molecule is

$$\int_{V_0}^{\infty} V_{01}\sigma_I(V_{01})\,g(V_{01})\,dV_{01} \qquad \text{(II-35)}$$

as of course it should be.

We may now obtain an approximation to the rate coefficient $\kappa(n,m|i,j)$ for those $(X^+ + e)$ - Z collisions in which the electron changes from an orbit or principal quantum number n to one of principal quantum number m and in which the molecule changes from level i of energy $\epsilon_i k\theta$ to level j of energy $\epsilon_j k\theta$ with

$$\epsilon_j - \epsilon_i = \nu. \qquad \text{(II-36)}$$

Following the procedure adopted by Bates and Khare (1965) we have that

$$\kappa(n,m|i,j) = \{\kappa_A(n,m|i,j)\,\kappa'_A(n,m|i,j)\}^{\frac{1}{2}}, \qquad \text{(II-37)}$$

where if we put
$$\lambda_1 \equiv e^2/2n^2a_0k\theta, \quad \lambda_2 \equiv e^2/2m^2a_0k\theta, \qquad \text{(II-38)}$$

then

$$\kappa_A(n,m|i,j) \equiv \frac{e^2}{a_0m^3k\theta}\kappa_A(\lambda_1,\lambda_2) \qquad \text{(II-39)}$$

and

$$\kappa'_A(n,m|i,j) \equiv \frac{\omega_j m^2}{\omega_i n^2}\exp(\lambda_2-\lambda_1-\nu)\,\kappa_A(m,n|j,i), \qquad \text{(II-40)}$$

ω_i and ω_j being the statistical weights of the levels indicated.

Averaging over the initial levels i and summing over the final levels j we see that the rate coefficient sought is

$$\kappa(n,m) = \kappa_0(n,m) + \kappa_\Sigma(n,m), \qquad \text{(II-41)}$$

where $\kappa_0(n,m)$ is the contribution from elastic scattering* (see Bates and Khare 1965) and where

*The simple expression which Bates and Khare gave for $\kappa_0(n,m)$ may be recovered from our expression for $\kappa(n,m|i,j)$ by carrying through some elementary analyses.

$$\kappa_{\chi}(n,m) = \frac{1}{f_Z(\theta)} \sum_i \sum_{j \neq i} \omega_i \exp(-\epsilon_i) \kappa(n,m|i,j) \qquad \text{(II-42)}$$

is the contribution from inelastic e-Z scattering, $f_z(\theta)$ being the internal partition function of the molecule. We shall denote the contributions to $\kappa_X(n,m)$ from rotational and vibrational transitions by $\kappa_R(n,m)$ and $\kappa_V(n,m)$ respectively. The letters affixed as subscripts to κ's will also be affixed to other quantities.

Examination of equations (II-30) to (II-32) shows that the rate coefficients are sensitive to the net change in the internal energy of the complex consisting of the recombining system and the third body. Anticipating the results of the detailed calculations we illustrate this in Table II-2. As would be expected physically the resonance effect exhibited becomes sharper as the temperature θ is decreased or as the reduced mass M_{XZ} is increased. Irregularities in the variation of the collisional conductance $\mathscr{G}(q)$ with q are evident in some of the tables to be presented later. These are due to resonances.

2. Method of Dalidchik and Sayasov

According to the classical diffusion method of Pitaevskii (1962) the recombination coefficient is given by

$$\alpha = \frac{e^6}{4}\left(\frac{\pi}{k\theta}\right)^{\frac{1}{2}}\left[\int_{-\infty}^{0} \frac{|E|^{\frac{1}{2}} \exp(E/k\theta)\, dE}{\mathscr{F}(E)}\right]^{-1} \qquad \text{(II-43)}$$

where $\mathscr{F}(E)$ is the mean of the square of the change in the energy E of the electron per unit time.

Pitaevskii considered only elastic collisions. Taking the scattering to be isotropic and the cross-section to have the constant value σ he demonstrated that

$$\mathscr{F}_0(E) = N(Z)\left\{\frac{64(2m_e)^{\frac{1}{2}}\sigma k\theta |E|^{\frac{1}{2}}}{3\pi M_{XZ}}\right\}. \qquad \text{(II-44)}$$

TABLE II-2. RESONANCE EFFECT IN ROTATIONAL TRANSITIONS OF HYDROGEN

temperature, θ/K	rotational quantum number, J	ion mass/a.m.u. 2	4	8	∞
		$\kappa(20,11\|J,J+2)$/cm^{3}s^{-1}			
250	0	7.7^{-14}	4.5^{-14}	3.1^{-14}	1.9^{-14}
	1	1.1^{-11}	1.0^{-11}	9.5^{-12}	8.8^{-12}
	2	2.0^{-14}	1.3^{-14}	9.5^{-15}	6.3^{-15}
500	0	1.4^{-13}	9.9^{-14}	7.6^{-14}	5.3^{-14}
	1	1.1^{-11}	1.1^{-11}	1.1^{-11}	1.0^{-11}
	2	6.4^{-14}	4.6^{-14}	3.7^{-14}	2.7^{-14}
1000	0	2.5^{-13}	1.9^{-13}	1.5^{-13}	1.2^{-13}
	1	1.0^{-11}	1.1^{-11}	1.1^{-11}	1.1^{-11}
	2	1.4^{-13}	1.1^{-13}	9.3^{-14}	7.5^{-14}
2000	0	4.1^{-13}	3.3^{-13}	2.8^{-13}	2.3^{-13}
	1	8.6^{-12}	9.3^{-13}	9.7^{-12}	1.0^{-11}
	2	2.6^{-13}	2.1^{-13}	1.8^{-13}	1.5^{-13}

Notes. The internal energy lost by the recombining system in the (20, 11) transition is $910k$ where k is the value of the Boltzmann constant (per kelvin); the internal energy gained by the H_2 molecule in the $(J, J+2)$ transition is $525k$, $875k$ and $1225k$ for $J = 0$, 1 and 2. The indices give the powers of 10 by which the entries should be multiplied.

Dalidchik and Sayasov (1966) showed how to take rotational transitions into account. For homopolar molecules they used the Born approximation to the cross-section concerned which has a very simple form (Gerjuoy and Stein 1955). Elementary analyses then yields

$$\mathscr{F}_R(E) = N(Z)\left\{\frac{1024Bq^2a_0^2k\theta|E|^{\frac{1}{2}}}{45(2m_e)^{\frac{1}{2}}}\right\}, \qquad \text{(II-45)}^*$$

where B is the rotational constant of the molecule and qea_0^2 is the quadrupole moment. The contributions $\mathscr{F}_0(E)$ and $\mathscr{F}_R(E)$ to $\mathscr{F}(E)$ are of course additive. Dalidchik and Sayasov (1967) also treated linear molecules having a permanent dipole moment. Taking the cross-section for rotational excitation to be as given by the Born approximation (Takayanagi 1966) they found that

$$\mathscr{F}_R(E) = N(Z)\left\{\frac{256(2m_e)^{\frac{1}{2}}Bd^2e^2k\theta}{9\hbar^2|E|^{\frac{1}{2}}}\ln\left(2\sqrt{\frac{k\theta}{B}}\right)\right\} \qquad \text{(II-46)}$$

dea_0 being the dipole moment. Where necessary we shall distinguish between $\mathscr{F}_R(E)$ of (II-45) and (II-46) by adding the letters q and d as subscripts.

Comparing (II-44), (II-45) and (II-46) it is seen that collisions involving rotational transitions are predicted to become increasingly more effective than elastic collisions as the energy of the electron is reduced. This prediction is in conflict with what might be expected from simple physical considerations and with the results of the semi-quantal theory. The error in the prediction, which is not of great importance in

*This is twice the value given by Dalidchik and Sayasov (1966) who omitted to allow for level J being (2J+1)-fold degenerate.

practice, arises because of the treatment of Dalidchik and Sayasov does not take fully into account the existence of a threshold energy for rotational excitation.

The mean of the square of the change in E per unit time due to vibrational transitions, $\mathcal{F}_V(E)$, was not discussed by Dalidchik and Sayasov. There is unlikely to be a simple analytical expression for it which is accurate enough to be useful. However, if the relevant excitation cross sections and energies are known $\mathcal{F}_V(E)$ may of course be obtained by carrying through the necessary integration numerically.

3. Calculations

Calculations were carried out relating to recombination in the presence of hydrogen, nitrogen, carbon dioxide and water vapor. All contributing processes in hydrogen and nitrogen were investigated. Attention was however concentrated on the contribution from vibrational transitions in the case of carbon dioxide and on that from rotational transitions in the case of water vapor. These are of interest in connection with recombination in gas mixtures.

We shall first briefly indicate the assumptions made about the relevant molecular properties.

The structural parameters were taken from the books by Herzberg (1945, 1950) or from references cited in them. The quadrupole moment of H_2 is $0.393ea_0^2$ (Harrick and Ramsey 1952) and that of N_2 is $0.96ea_0^2$ (Smith and Howard 1950); the dipole moment of H_2O is $0.736ea_0$ (McClellan 1963).

The elastic scattering cross-sections of H_2 and N_2 towards slow electrons were put equal to $30a_0^2$ and $15a_0^2$ respectively (Moiseiwitsch 1962). Elastic scattering by H_2O was disregarded since scattering by a rotating dipole is predominantly inelastic (Crawford, Dalgarno and Hays 1967).

The values adopted for the rotational excitation cross-sections of H_2 and N_2 were those given by the distorted wave approximation (Takayanagi and Geltman 1965). In the case of H_2 these are much larger than

the cross-sections given by the Born approximation (Gerjuoy and Stein 1955), but in the case of N_2 the two cross-sections do not differ greatly. The rotational excitation cross-sections of H_2O were obtained by substituting the line strengths calculated by Cross, Hainer and King (1944) into the formula which Crawford (1967) derived for asymmetric top molecules using the Born approximation. Dalidchik and Sayasov (1967) took H_2O to be a linear dipole molecule having a moment of inertia equal to the smallest of the three principal moments. Calculations which we have carried out on the collisional conductances show that this is quite a good approximation.

The cross-sections for the vibrational excitation of H_2 and CO_2 were taken from measurements by Schulz (1964)* and by Boness and Schulz (1968) respectively; those for the vibrational excitation of N_2 were taken from the theoretical investigation by Chen (1964). Reliable information on the vibrational excitation of H_2O is not available. Takayanagi (1966) has suggested that in the case of a linear molecule the cross-section is approximately

$$\sigma(v, J \to v+1, J+1) = \frac{2\pi d^2 (v+1) J_>}{3E\bar{M}R_e^2 I_V (2J+1)} \ln \frac{4E}{I_V} \qquad \text{(II-47)}$$

in which $\bar{M}$ is the reduced mass of the vibrating atoms, R_e is the equilibrium internuclear distance, I_V is the vibrational quanta, the other symbols have their usual significance and all quantities are in atomic units. Tentatively adopting this formula for each of the vibrational modes we rather arbitrarily set $\bar{M} R_e^2$ equal to 3 M_p where M_p is the mass of the proton and took the rotational energy levels to be as in the model used by Dalidchik and Sayasov (1967).

The distance r_0 introduced in (II-16) is ill defined. We took it to be 0.1 nm. Fortunately the results are insensitive to the value chosen.

Little need be said about the numerical procedure which is straightforward. Care is needed in carrying out the quadrature in (II-31) because

*Following a private communication from Dr. Schulz, the threshold energy of 1.0 eV originally reported was modified to 0.53 eV but the overall pattern of the variation of the cross section was retained.

of the sharp peak exhibited by the integrand. Severe cancellation occurs between the error functions in (II-32) so that they must be represented very accurately. We used the 22-term even Chebyshev series for $4x^{-1}$ erfx through the region in which the independent variable x is less than 4.0 and used the 9-term even Chebyshev series for $\pi^{\frac{1}{2}}x\exp(x^2)\mathrm{erfc}\,x$ elsewhere (Clenshaw 1963).

Transitions involving levels for which q is very high, say above some value q_1, are caused mainly by elastic collisions (except in the case of polar molecules). It is sometimes convenient to treat them by the method of Pitaevskii (1962). This simplifies the evaluation of the infinite summation appearing in (II-6): thus we obtain

$$\sum_{q=q_0+1}^{\infty}\frac{\mu(q)}{\mathscr{C}(q)+\mathscr{A}(q)}=\left\{\sum_{q=q_0+1}^{q_1}\frac{\mu(q)}{\mathscr{C}(q)+\mathscr{A}(q)}\right\}+P(q_1), \qquad \text{(II-48)}$$

where

$$P(q_1)=\frac{3M_{XZ}h^3k\theta}{64\pi^2m_e^2e^6\sigma N(Z)}\left\{1-\left[1+\frac{e^2}{2q_1^2a_0k\theta}\right]\exp\left(-\frac{e^2}{2q_1^2a_0k\theta}\right)\right\}. \qquad \text{(II-49)}$$

4. Results and Discussion

a. Hydrogen

Figures II-1 and II-2 show the results obtained on the recombination of an ion of atomic mass 2 in molecular hydrogen. The values of the recombination coefficient, $\alpha'_{CR}(2,H_2)$ are very high. They greatly exceed those for $\alpha'_{CR}(4,He)$ as calculated by Bates and Khare (1965). Thus if the ambient number density is 3×10^{19} cm^{-3}, $\alpha'_{CR}(2,H_2)$ is 8×10^{-7} cm^3 s^{-1} at 250 K and is 8×10^{-9} cm^3 s^{-1} at 2000 K, whereas the corresponding values for $\alpha'_{CR}(4,He)$ are 5×10^{-8} cm^3 s^{-1} and 2×10^{-11} cm^3 s^{-1}. There are two main reasons for the difference: the reduced mass of the ion and third body is less in the first case than in the second; and the cross-section of an H_2 molecule for the elastic scattering of slow electrons is greater than that of an He atom. As the temperature is raised the contribution to $\alpha'_{CR}(2,H_2)$ from rotational and vibrational transitions increases in importance (Figure II-2).

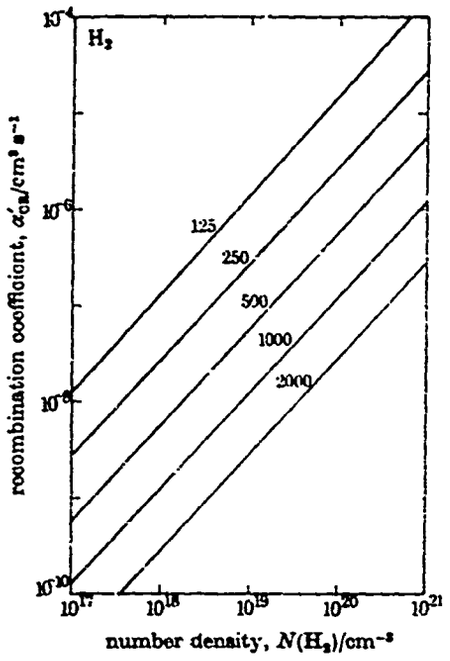

Figure II-1. Recombination coefficient α'_{cR} for $Z^+ + e + H_2 \rightarrow Z + H_2$ as function of the hydrogen molecule number density. The temperature θ(K) is indicated on each curve. The mass of the ion is taken to be 2 a.m.u.

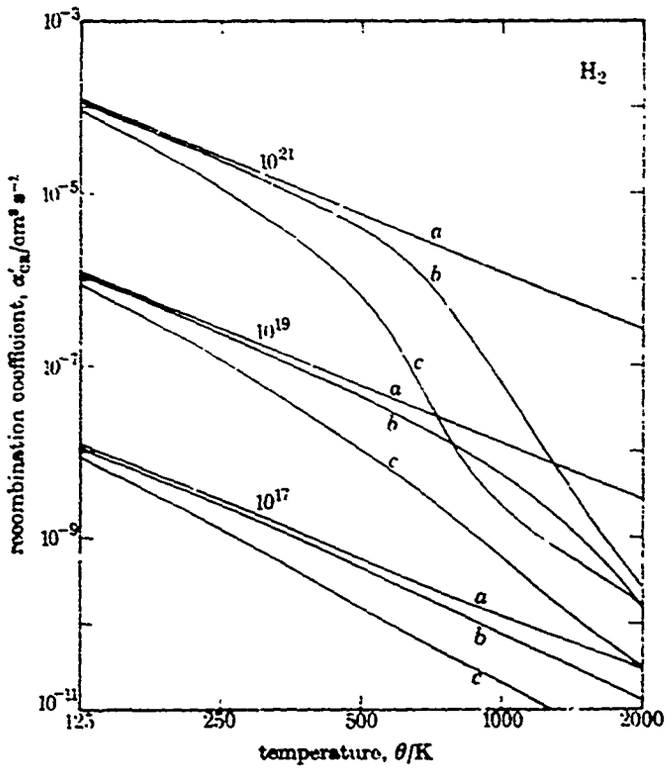

Figure II-2. Recombination coefficient α'_{cR} for $Z^+ + e + H_2 \rightarrow Z + H_2$ as function of the temperature. The hydrogen molecule number density $N(H_2)$ (cm^{-3}) is indicated on each set of curves. The mass of the ion is taken to be 2 a.m.u. Curve *a*, all types of transition included; curve *b*, vibrational transitions excluded; curve *c*, vibrational and rotational transitions excluded.

Table II-3 provides information on the recombination mechanism in the form suggested by Bates & Khare. It gives (i) the critical principal quantum number q_X at which the term

$$t_q = \frac{\mu(q)}{\mathscr{C}(q)+\mathscr{A}(q)} \qquad \text{(II-50)}$$

of the summation in (II-7) is greatest; (ii) the values, $q_{\frac{1}{2}X^-}$ and $q_{\frac{1}{2}X^+}$ of q below and above q_X at which t(q) is closest to $\frac{1}{2}t(q_X)$; (iii) the actual ratios

$$r_{\frac{1}{2}X^-} = t(q_{\frac{1}{2}X^-})/t(q_X), \quad r_{\frac{1}{2}X^+} = t(q_{\frac{1}{2}X^+})/t(q_X), \qquad \text{(II-51)}$$

and (iv) the ratios $\mu(q_{\frac{1}{2}X^- - 1})$, $\mu(q_X - 1)$ and $\mu(q_{\frac{1}{2}X^+ - 1})$where $\mu(a)$ is as defined in (II-6) so that the extent to which these ratios fall below unity indicates the importance of radiative transitions. Rotational and vibrational transitions make q_X larger than it is for helium. Moreover, they keep radiative transitions insignificant, whereas in the case of helium such transitions have a marked effect at the lower densities and high temperatures studied.

For comparison some calculations were carried out by the classical diffusion method. A trifling modification was made to the formula of Dalidchik and Sayasov (1966): the evaluation of $\mathscr{F}_{Rq}(E)$ was carried through without the simplifying assumption, which leads to (II-45), that the rotational constant B is very much smaller than $k\theta$, this assumption being invalid at the lower temperatures of interest in the case of hydrogen. In fact the modification had little influence on the final results. The derived values of some of the recombination coefficients are given in Table II-4 together with the corresponding values obtained by the semi-quantal method. To avoid complicating the comparison these last are also based on the Born approximation to the rotational cross sections and do not include the contribution from vibrational transitions. As would be expected the classical diffusion method gives larger recombination coefficients because of the assumption that the negative energy levels of

TABLE II-3. RECOMBINATION MECHANISM FOR IONS OF ATOMIC MASS 2 IN MOLECULAR HYDROGEN

temperature, θ/K			
	19	25	>35
125	0.50		~0.5
	1.0	1.0	1.0
	12	(16, 21)	>30
250	0.50		~0.5
	1.0	1.0	1.0
	8	11	21
500	0.66		0.51
	0.97	1.0	1.0
	6	8	15
1000	0.43		0.45
	0.95	0.99	1.0
	4	7	11
2000	0.58		0.53
	0.94	0.99	1.0

The entries for each temperature are almost independent of the number density $N(H_2)$ provided this is not below about $10^{17}\,cm^{-3}$. They are arranged in the form

$q_{\frac{1}{2}X^-}$	q_X	$q_{\frac{1}{2}X^+}$
$r_{\frac{1}{2}X^-}$		$r_{\frac{1}{2}X^+}$
$\mu(q_{\frac{1}{2}X^-}-1)$	$\mu(q_X-1)$	$\mu(q_{\frac{1}{2}X^+}-1)$

the notation being as defined in the text.

TABLE II-4. COMPARISON OF VALUES OF RECOMBINATION COEFFICIENT OBTAINED BY CLASSICAL DIFFUSION AND SEMI-QUANTAL METHOD FOR IONS OF ATOMIC MASS 2 IN MOLECULAR HYDROGEN

		temperature, θ/K		
$N(H_2)$/cm^{-3}		125	500	2000
10^{17}	(i)	2.6^{-6}	5.5^{-10}	1.3^{-11}
	(ii)	1.0^{-5}	2.8^{-10}	5.6^{-13}
10^{19}	(i)	2.6^{-6}	5.5^{-9}	1.3^{-9}
	(ii)	1.6^{-6}	2.6^{-8}	1.0^{-10}
10^{21}	(i)	2.6^{-4}	5.5^{-6}	1.3^{-7}
	(ii)	1.0^{-4}	1.5^{-6}	1.8^{-10}

Notes. (i) indicates the classical diffusion method and (ii) the semi-quantal method using same cross-sections (see text). Vibrational transitions are ignored.

The indices give the powers of 10 by which the entries should be multiplied.

an ion form a continuum. The effect is especially marked when the density and temperature are high.

The results in Table II-5 show that an increase in M_X the mass of the ion from 2, on the chemical scale, to infinity causes the recombination coefficient to fall to about 30 to 40%. Their detailed pattern is rather complicated because of the variation with temperature of the relative importance of the three types of collision involved. A significant increase in M_X is normally accompanied by a change in the structure of the system and therefore by changes in the radiative and collisional conductances which are not taken into account in Table II-5. The radiative conductances are relatively unimportant (see Table II-3). Owing to resonance effects some of the rate coefficients which determine the collisional conductances may be greatly affected by the differences between the energies of the levels of X and the assumed hydrogenic values. The recombination coefficient is however, likely to be affected to only a minor extent since it depends (see Table II-3) on a considerable number of transitions. An upper limit to the recombination coefficient at a given temperature is provided by the classical diffusion method (provided the gas density is high enough for radiative transitions to be unimportant). The last row of Table II-5 shows the upper limits obtained using the elastic, rotational vibrational cross sections adapted in the calculations by the semi-quantal method, and evaluating $\mathcal{F}_R(E)$ and $\mathcal{F}_V(E)$ by numerical quadrature. The factor by which the upper limit exceeds the corresponding recombination coef-

TABLE II-5. INFLUENCE OF MASS M_X OF ION ON RECOMBINATION COEFFICIENT IN MOLECULAR HYDROGEN: $N(H_2) = 10^{19}$ cm^{-3}

	temperature, θ, K			
	250	500	1000	2000
	α'_{CR} cm^{3}s^{-1}			
M_X a.m.u.				
2	2.8^{-7}	5.7^{-8}	1.2^{-8}	2.8^{-9}
4	2.2^{-7}	5.0^{-8}	1.1^{-8}	2.5^{-9}
8	1.9^{-7}	4.5^{-8}	1.0^{-8}	2.4^{-9}
∞	1.7^{-7}	4.2^{-8}	9.2^{-9}	2.0^{-9}
upper limit (classical diffusion method):				
M_X infinite	1.0^{-6}	2.7^{-7}	4.0^{-8}	5.3^{-9}

The indices give the powers of 10 by which the entries should be multiplied.

ficient decreases as the temperature is increased. This is because the inhibiting effect of lack of balance between the initial and final internal energies of the colliding systems is less marked at high temperatures than at low temperatures.

The recombination coefficient in a mixture of neutral gases is not the sum of the recombination coefficients in each of the constituent gases. However, the collisional conductances are additive; and using formula (II-7) the recombination coefficient may readily by obtained from these and the radiative conductances (see § 2 in particular Table II-1).

The important collisional conductances for molecular hydrogen are given in Table II-6. Except near a resonance they are decreasing functions of the ion mass.

TABLE II-6. COLLISIONAL CONDUCTANCES IN HYDROGEN†

quantum level q	temperature, θ/K: 250	500	1000	2900
	$\mathscr{C}(q)/N(H_2)$/s^{-1}			
	ion mass 2 a.m.u.			
4	4.8^{+3}	2.6^{-3}	8.3^{-6}	5.0^{-7}
5	1.1^{+2}	1.9^{-3}	8.6^{-6}	7.3^{-7}
6	3.2^{-2}	4.3^{-5}	2.0^{-6}	6.4^{-7}
7	3.0^{-3}	8.4^{-6}	9.8^{-7}	5.4^{-7}
8	1.9^{-4}	3.3^{-6}	9.1^{-7}	6.0^{-7}
9	1.2^{-4}	3.3^{-6}	1.0^{-6}	7.3^{-7}
10	5.6^{-5}	3.0^{-6}	1.2^{-6}	8.8^{-7}
11	1.2^{-5}	2.2^{-6}	1.2^{-6}	1.0^{-6}
12	1.1^{-5}	2.4^{-6}	1.4^{-6}	1.2^{-6}
13	7.2^{-6}	2.5^{-6}	1.6^{-6}	1.5^{-6}
14	7.2^{-6}	2.6^{-6}	1.8^{-6}	1.8^{-6}
15	7.0^{-6}	2.8^{-6}	2.0^{-6}	2.2^{-6}
16	5.7^{-6}	2.8^{-6}	2.3^{-6}	2.8^{-6}
17	5.9^{-6}	3.0^{-6}	2.7^{-6}	3.4^{-6}
18	5.9^{-6}	3.3^{-6}	3.1^{-6}	4.2^{-6}
19	5.9^{-6}	3.6^{-6}	3.7^{-6}	5.1^{-6}
20	5.6^{-6}	3.9^{-6}	4.3^{-6}	6.2^{-6}
21	5.6^{-6}	4.3^{-6}	5.0^{-6}	—
22	5.8^{-6}	4.9^{-6}	—	—
23	6.1^{-6}	—	—	—

quantum level q	temperature, θ/K: 250	500	1000	2000
	$\mathscr{C}(q)/N(H_2)$/s^{-1}			
	ion mass 4 a.m.u.			
4	2.1^{+2}	1.4^{-3}	6.5^{-6}	4.5^{-7}
5	5.1^{+1}	1.3^{-3}	7.0^{-6}	6.5^{-7}
6	2.3^{-2}	3.7^{-5}	1.8^{-6}	6.2^{-7}
7	2.5^{-3}	7.3^{-6}	9.2^{-7}	5.3^{-7}
8	1.6^{-4}	3.0^{-6}	9.0^{-7}	5.9^{-7}
9	1.2^{-4}	3.3^{-6}	1.0^{-6}	7.1^{-7}
10	5.8^{-5}	3.0^{-6}	1.1^{-6}	8.3^{-7}
	ion mass 8 a.m.u.			
4	3.9^{+1}	9.4^{-4}	5.5^{-6}	4.1^{-7}
5	2.7^{+1}	9.2^{-4}	5.9^{-6}	6.0^{-7}
6	2.0^{-2}	2.7^{-5}	1.7^{-6}	6.0^{-7}
7	2.2^{-3}	6.7^{-6}	9.0^{-7}	5.3^{-7}
8	1.4^{-4}	2.7^{-6}	8.9^{-7}	5.9^{-7}
9	1.3^{-4}	3.3^{-6}	1.0^{-6}	7.9^{-7}
10	6.0^{-5}	3.0^{-6}	1.1^{-6}	8.0^{-7}
	ion mass infinite			
4	1.1^{+1}	5.6^{-4}	4.3^{-6}	3.5^{-7}
5	1.0^{+1}	5.6^{-4}	4.6^{-6}	5.0^{-7}
6	1.8^{-2}	3.3^{-5}	1.6^{-6}	5.9^{-7}
7	1.9^{-3}	6.4^{-6}	8.8^{-7}	5.3^{-7}
8	1.2^{-4}	2.8^{-6}	9.0^{-7}	6.0^{-7}
9	1.4^{-4}	4.0^{-6}	1.0^{-6}	7.0^{-7}
10	6.3^{-5}	3.7^{-6}	1.1^{-6}	7.9^{-7}

† More extensive tables are given by Malaviya (1970).
The indices give the powers of 10 by which the entries should be multiplied.

b. Nitrogen and Carbon Dioxide

Results of calculations on $\alpha'_{CR}(28|N_2)$ by the semi-quantal method, with the radiative conductance taken to be $f(2)\mathscr{A}(q|H)$ of Table II-1 are displayed in Figure II-3 along lines of constant temperature. Figure II-4 shows some of the same results along lines of constant density and also shows the effect of neglecting vibrational transitions. For comparison purposes results of calculations using formulae (II-43) and (II-45) of the classical diffusion method are included in this figure.

As may be seen collisional radiative recombination in nitrogen is much slower than in hydrogen. There are two main reasons for the difference. First, elastic collisions are unimportant in the case of nitrogen because of the molecules being so massive, whereas they are quite significant in the case of hydrogen. Secondly the rotational constant B is considerably smaller for nitrogen than for hydrogen which renders the rotational transitions less effective (see Figures II-2 and II-4).

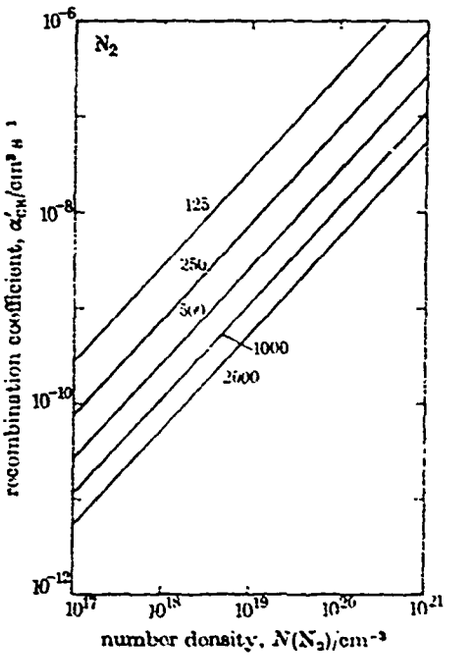

Figure II-3. Recombination coefficient α'_{CR} for $Z^+ + e + N_2 \rightarrow Z + N_2$ as function of the nitrogen molecule number density. The temperature θ(K) is indicated on each curve. The mass of the ion is taken to be 28 a.m.u.

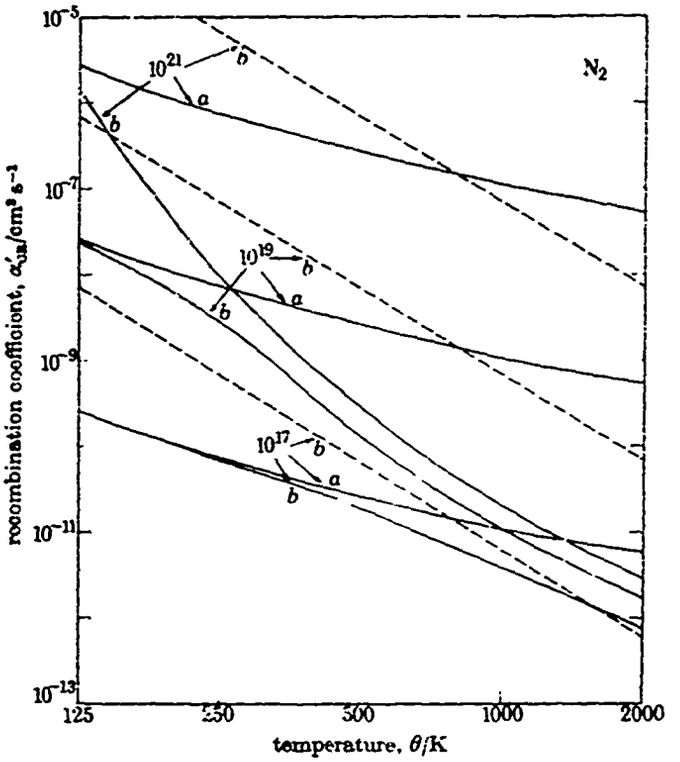

Figure II-4. Recombination coefficient α'_{ca} for $Z^- + e + N_2 \rightarrow Z + N_2$ as function of the temperature. The nitrogen molecule number density $N(N_2)$ is indicated on each curve. The mass of the ion is taken to be 28 a.m.u. Curve *a*, all types of transition included; curve *b*, vibrational transitions excluded (full line, semi-quantal; broken line, classical diffusion).

The results obtained by the classical diffusion method differ markedly from the results obtained by the semi-quantal method (Figure II-4). This is because the main resistance to the down-flow of the recombining electrons arises from the wide gaps (ignored in the classical diffusion method) between the levels of low principal quantum number. These gaps are mainly bridged by collisions involving vibrational transitions (Figure II-4).

Table II-7 shows how the recombination coefficient derived using the semi-quantal method depends on the mass M_X of the ion. If M_X is expressed in units of the mass of the molecule the dependence is rather similar to that for hydrogen (Table II-5). To regard M_X as a quantity which may be varied in isolation is of course artificial. The remarks made in this connection towards the end of 3 are relevant. Little guidance

TABLE II-7. INFLUENCE OF MASS M_X OF ION ON RECOMBINATION COEFFICIENT IN MOLECULAR NITROGEN: $N(N_2) = 10^{19}$ cm^{-3}

	temperature, θ/K			
	250	500	1000	2000
M_X/a.m.u.	α'_{CR}/cm^{3}s^{-1}			
7	1.7^{-8}	5.3^{-9}	1.8^{-9}	8.1^{-10}
14	1.1^{-8}	3.7^{-9}	1.4^{-9}	6.6^{-10}
28	7.6^{-9}	2.7^{-9}	1.1^{-9}	5.5^{-10}
56	5.8^{-9}	2.1^{-9}	9.4^{-10}	4.7^{-10}
112	4.8^{-9}	1.8^{-9}	8.2^{-10}	4.2^{-10}
upper limit (classical diffusion method): M_X infinite	2.4^{-6}	3.8^{-7}	5.7^{-8}	7.2^{-9}

The indices give the powers of 10 by which the entries should be multiplied.

is provided by the upper limits obtained from the classical diffusion method. These are given in the last row of Table II-7. Each is very much greater than the corresponding value of the recombination coefficient calculated using the semi-quantal method. This is mainly because of the closeness of the molecular energy levels and the largeness of the reduced mass.

Collisional-radiative recombination in pure nitrogen gas is too slow to be of much interest. Instead of presenting further results on the rate of this process we give in Table II-8 some collisional conductances which may be required in calculations on recombination in gas mixtures containing nitrogen.

In the case of carbon dioxide collisional conductances have been computed for the lower levels where vibrational transitions dominate. The values obtained have been tabulated by Malaviya (1970). They are smaller than the corresponding values for nitrogen and will not be given here.

c. Water Vapor and Damp Gases

Table II-9 contains a selection of the calculated rotational contributions to the collisional conductances of water vapor. Most are

TABLE II-8. COLLISIONAL CONDUCTANCES IN NITROGEN†

quantum level q	temperature, θ/K: 250	500	1000	2000
	$\mathscr{G}(q)/N(N_2)/s^{-1}$			
	ion mass 7 a.m.u.			
4	2.4^{+1}	2.7^{-3}	2.3^{-5}	1.6^{-5}
5	8.9^{+1}	4.4^{-3}	3.6^{-5}	2.7^{-6}
6	2.4^{+1}	2.8^{-3}	2.7^{-5}	2.2^{-6}
7	1.0^{-1}	1.3^{-4}	4.3^{-6}	7.4^{-7}
8	2.2^{-6}	3.4^{-7}	1.5^{-7}	1.5^{-7}
9	2.2^{-6}	3.4^{-7}	1.6^{-7}	1.6^{-7}
10	2.2^{-6}	3.7^{-7}	1.9^{-7}	1.8^{-7}
	ion mass 14 a.m.u.			
4	3.1^{-1}	3.5^{-3}	3.0^{-5}	2.7^{-6}
5	3.5^{-1}	4.0^{-3}	3.9^{-5}	3.9^{-6}
6	3.1^{-1}	3.6^{-3}	3.5^{-5}	3.5^{-6}
7	1.2^{-1}	1.6^{-4}	5.1^{-6}	9.3^{-7}
8	1.4^{-6}	2.8^{-7}	1.4^{-7}	1.3^{-7}
9	1.4^{-6}	2.6^{-7}	1.5^{-7}	1.5^{-7}
10	1.4^{-6}	3.0^{-7}	1.8^{-7}	1.7^{-7}
	ion mass 28 a.m.u.			
4	3.6^{+1}	4.2^{-3}	3.6^{-5}	3.2^{-6}
5	3.7^{+1}	4.4^{-3}	4.3^{-5}	4.4^{-6}
6	3.7^{+1}	4.4^{-3}	4.2^{-5}	4.2^{-6}
7	1.3^{-1}	1.8^{-4}	5.8^{-6}	1.0^{-6}
8	3.6^{-7}	2.2^{-7}	1.3^{-7}	1.3^{-7}
9	3.6^{-7}	2.2^{-7}	1.3^{-7}	1.5^{-7}
10	3.6^{-7}	2.4^{-7}	1.6^{-7}	1.6^{-7}
11	1.1^{-6}	3.3^{-7}	2.0^{-7}	1.9^{-7}
12	1.3^{-6}	3.6^{-7}	2.1^{-7}	2.2^{-7}

quantum level q	temperature, θ/K: 250	500	1000	2000
	$\mathscr{G}(q)/N(N_2)/s^{-1}$			
	ion mass 28 a.m.u. (*cont.*)			
13	6.4^{-7}	2.1^{-7}	1.6^{-7}	2.0^{-7}
14	5.6^{-7}	2.1^{-7}	2.0^{-7}	2.8^{-7}
15	4.9^{-7}	2.7^{-7}	2.9^{-7}	4.4^{-7}
16	9.1^{-7}	4.2^{-7}	4.4^{-7}	6.6^{-7}
17	9.0^{-7}	5.7^{-7}	6.4^{-7}	9.2^{-7}
18	1.0^{-6}	7.4^{-7}	9.0^{-7}	—
19	1.2^{-6}	9.5^{-7}	—	—
20	1.3^{-6}	—	—	—
	ion mass 56 a.m.u.			
4	4.1^{+1}	4.8^{-3}	4.2^{-5}	2.8^{-6}
5	4.1^{+1}	5.0^{-3}	4.9^{-5}	3.8^{-6}
6	4.1^{-1}	5.0^{-3}	4.8^{-5}	3.7^{-6}
7	1.3^{-1}	1.9^{-4}	6.3^{-6}	1.0^{-6}
8	5.5^{-7}	1.7^{-7}	1.1^{-7}	1.2^{-7}
9	5.5^{-7}	1.7^{-7}	1.2^{-7}	1.3^{-7}
10	5.5^{-7}	1.9^{-7}	1.5^{-7}	1.5^{-7}
	ion mass 112 a.m.u.			
4	4.4^{+1}	5.2^{-3}	4.5^{-5}	3.1^{-6}
5	4.4^{+1}	5.4^{-3}	5.2^{-5}	4.1^{-6}
6	4.4^{+1}	5.4^{-3}	5.2^{-5}	4.0^{-6}
7	1.3^{-1}	2.0^{-4}	6.6^{-6}	1.1^{-6}
8	3.9^{-7}	1.4^{-7}	1.1^{-7}	1.1^{-7}
9	3.9^{-7}	1.4^{-7}	1.1^{-7}	1.3^{-7}
10	3.9^{-7}	1.6^{-7}	1.4^{-7}	1.5^{-7}

† More extensive tables are given by Malaviya (1970).
The indices give the powers of 10 by which the entries should be multiplied.

several powers of ten greater than the corresponding total collisional conductances of non-polar gases.

Using formula (II-47) the vibrational contributions at the lower principal quantum numbers were computed. They were found to be only moderate in magnitude. In treating gas mixtures like damp hydrogen or damp nitrogen, it is a sufficient approximation to replace the vibrational contribution from the water vapor by the vibrational contribution from an equal quantity of the major gas.

TABLE II-9. COLLISIONAL CONDUCTANCES IN WATER VAPOUR†

quantum level q	temperature, θ/K: 250	500	1000	2000
	$\mathscr{C}(q)/N(H_2O)/s^{-1}$			
	ion mass 9 a.m.u.			
6	6.0^{-12}	8.6^{-12}	6.2^{-12}	4.1^{-12}
7	2.5^{-8}	2.9^{-7}	2.4^{-8}	6.6^{-9}
8	1.6^{-4}	1.2^{-5}	8.0^{-6}	6.2^{-6}
9	1.6^{-3}	2.1^{-4}	5.6^{-5}	2.3^{-5}
10	4.8^{-3}	3.2^{-4}	7.2^{-5}	3.5^{-5}
11	2.0^{-3}	3.6^{-4}	1.6^{-4}	1.0^{-4}
12	3.4^{-3}	6.3^{-4}	2.7^{-4}	1.8^{-4}
13	2.9^{-3}	7.5^{-4}	4.0^{-4}	3.0^{-4}
14	4.5^{-3}	1.1^{-3}	6.8^{-4}	5.5^{-4}
15	3.6^{-3}	1.4^{-3}	1.0^{-3}	9.0^{-4}
	ion mass 18 a.m.u.			
6	3.3^{-12}	1.2^{-12}	1.1^{-12}	2.5^{-12}
7	2.5^{-8}	2.9^{-7}	2.4^{-8}	6.3^{-9}
8	1.6^{-4}	1.0^{-5}	7.2^{-6}	6.0^{-6}
9	1.6^{-3}	2.1^{-4}	5.7^{-5}	2.4^{-5}
10	4.8^{-3}	3.3^{-4}	7.5^{-5}	3.7^{-5}
11	1.7^{-3}	3.4^{-4}	1.6^{-4}	1.0^{-4}
12	3.1^{-3}	6.1^{-4}	2.7^{-4}	1.8^{-4}
13	2.8^{-3}	7.3^{-4}	4.1^{-4}	3.1^{-4}
14	4.5^{-3}	1.1^{-3}	6.8^{-4}	5.6^{-4}
15	3.5^{-3}	1.4^{-3}	1.0^{-3}	9.1^{-4}

quantum level q	temperature, θ/K: 250	500	1000	2000
	$\mathscr{C}(q)/N(H_2O)/s^{-1}$			
	ion mass 36 a.m.u.			
6	3.4^{-14}	2.4^{-14}	3.5^{-14}	9.1^{-14}
7	2.4^{-8}	2.8^{-7}	2.4^{-8}	6.1^{-9}
8	1.6^{-4}	9.5^{-6}	6.6^{-6}	5.8^{-6}
9	1.5^{-3}	2.1^{-4}	5.7^{-5}	2.5^{-5}
10	4.7^{-3}	3.3^{-4}	7.6^{-5}	3.8^{-5}
11	1.6^{-3}	3.2^{-4}	1.6^{-4}	1.0^{-4}
12	2.8^{-3}	5.8^{-4}	2.7^{-4}	1.8^{-4}
13	2.7^{-3}	7.2^{-4}	4.1^{-4}	3.1^{-4}
14	4.5^{-3}	1.1^{-3}	6.8^{-4}	5.6^{-4}
15	3.5^{-3}	1.4^{-3}	1.0^{-3}	9.1^{-4}

† More extensive tables are given by Malaviya (1970).
The indices give the powers of 10 by which the entries should be multiplied.

Figure II-5 shows the calculated collisional radiative recombination coefficients in some damp gases as functions of the percentage by volume of water vapor, a pressure of one atmosphere being maintained. As may be seen the presence of a small amount of water vapor increases the recombination coefficient markedly. The increase is due to the rise in the collisional conductances through levels of high principal quantum numbers (see Tables II-3 and II-10).

The classical diffusion method predicts faster recombination (especially at the lower temperatures) since substituting from (II-46) into (II-43) gives

$$\alpha \doteq 1.2 \times 10^{-25} N(H_2O) \left\{\frac{1000}{\theta}\right\}^{4.5} \lg\left(\frac{\theta}{10}\right) \text{cm}^3\text{s}^{-1}. \qquad \text{(II-52)}$$

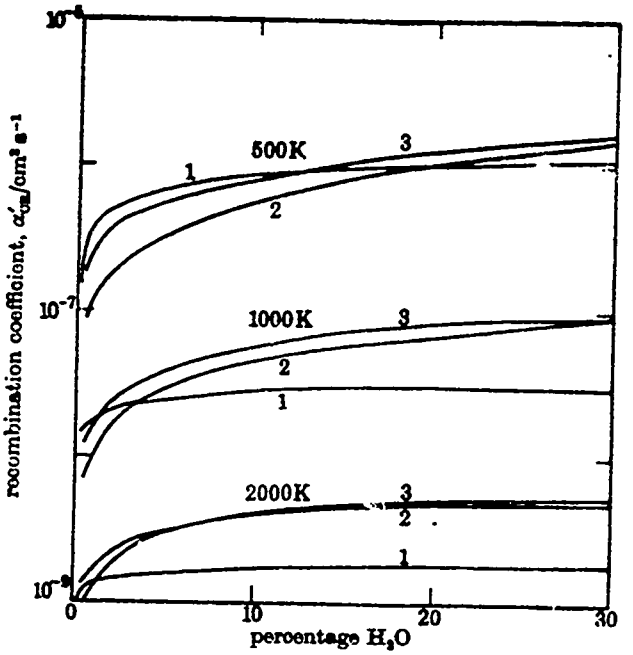

Figure II-5. Recombination coefficient α_{CR} in damp gas mixtures at atmospheric pressure as function of the percentage by volume of water vapour. The temperature θ(K) is indicated on each set of curves. The mass of the ion is taken to be 23 a.m.u. Curve 1, hydrogen; curve 2, nitrogen; curve 3, hydrogen–nitrogen ($[H_2]:[N_2]::1:2$).

TABLE II-10. RECOMBINATION MECHANISM FOR IONS OF ATOMIC MASS 23 IN A DAMP NITROGEN + HYDROGEN ($n(N_2):n(H_2)::2:1$) MIXTURE AT ATMOSPHERIC PRESSURE

temperature,	water vapour (%)					
	½			32		
θ/K	7	8	9	7	8	9
500	0.0		0.4	0.1		0.1
	1.0	1.0	1.0	1.0	1.0	1.0
	7	8	10	6	8	9
1000	0.1		0.5	0.1		0.1
	1.0	1.0	1.0	1.0	1.0	1.0
	7	S	9	6	7	9
2000	0.4		0.6	0.3		0.3
	1.0	1.0	1.0	1.0	1.0	1.0

The basic cause of the difference may be seen by considering the integrand of expression (II-43) for the recombination coefficient. It goes through a maximum, corresponding to the conductivity going through a minimum, where $|E|$ is $3k\theta$ which is where the principal quantum number q_m is 230θ-1/2 if the energy levels of X are hydrogenic. However, the semi-quantal calculations show that the rotational contribution to the collisional conductance does not begin to increase as q passes below 230θ-1/2; instead it continues to fall more and more steeply because of the widening separation between the energy levels. The collisional conductance does indeed increase; but this is due to the growth in the vibrational contribution. Formula (II-52) does not take the vibrational contribution into account which introduces an error in the opposite sense to that arising from the overestimation of the rotational contribution. Since the two errors are entirely unrelated they can scarcely, in general, approximately cancel.

The rate coefficients for the rotational transitions of water greatly exceed those for the vibrational transitions of hydrogen or nitrogen. Hence formula (II-52) gives an upper limit to the recombination coefficient provided the water vapor has not such low abundance relative to the main gas that it does not control the conductances on the outer side of the minimum. This upper limit is of interest in connection with the problem of recombination to complex ions which are such that the energy levels of X lie much closer together than the hydrogenic levels assumed in the semi-quantal calculations.

An experimental study of the decay of Pb^+ ions in flames at atmospheric pressure has been carried out by Hayhurst and Sugden (1955). Mass spectroscopic measurements showed that the ratio $[Pb^+]/[Pb^+.H_2O]$ was about 300 which enabled Hayhurst and Sugden to dismiss the dissociative recombination process

$$Pb^+.H_2O + e \rightarrow Pb + H_2O \qquad \text{(II-53)}$$

and to infer that the decay was caused by recombination following a collision between an electron and a neutral molecule, probably H_2O as in

$$Pb^+ + e + H_2O \rightarrow Pb + H_2O. \qquad \text{(II-54)}$$

Their results, expressed as effective binary recombination coefficients, are given in Table II-11 where they are compared with the corresponding result obtained by the semi-quantal method and by the classical diffusion method. It may be seen that the measured values of the recombination coefficient are straddled by the calculated values in the predicted manner. In view of the ion concerned it is reasonable that they should lie closer to the upper limit than to the lower limit.

Kelly and Padley (1969) have investigated the decay of Ga^+, In^+ and Tl^+ ions in flames at atmospheric pressure. In accordance with the theory the recombination coefficients obtained for these heavy ions did not differ significantly from each other or from the recombination coefficients for Pb^+ ions (Table II-11).

Unfortunately direct determinations have not been made of the recombination coefficients for Na^+ or other light ions the parent atoms of which are nearly hydrogenic. However, there have been studies (Hayhurst and Sugden 1965, 1967; Kelly and Padley 1969) of the growth of the ionization of alkali atoms in flames at atmospheric pressure. The growth is attributed to processes like

TABLE II-11. RECOMBINATION COEFFICIENTS FOR Pb^+ IONS IN DAMP NITROGEN–HYDROGEN MIXTURES AT ATMOSPHERIC PRESSURE

temperature, θ/K	composition of mixture† volume percentage			recombination coefficient cm^3s^{-1}		
					calculated	
	N_2	H_2	H_2O	measured†	lower limit	upper limit
1680	67	14	19	2.1^{-7}	9.2^{-9}	2.2^{-7}
1785	63	16	21	1.2^{-7}	8.0^{-9}	1.7^{-7}
1800	63	16	21	1.3^{-7}	7.0^{-9}	1.6^{-7}
2005	50	25	25	8.1^{-9}	4.1^{-9}	1.1^{-8}
2010	50	25	25	6.2^{-9}	4.0^{-9}	1.1^{-8}
2260	47	23	30	6.1^{-9}	3.1^{-9}	6.9^{-9}
2270	47	23	30	6.1^{-9}	3.0^{-9}	6.8^{-9}

† The temperature, the recombination coefficient and the percentage of water vapour are given in Hayhurst & Sugden (1965); other information on the composition is given in Hayhurst & Sugden (1966, 1967).

The indices give the powers of 10 by which the entries should be multiplied.

$$Na + H_2O \rightarrow Na^+ + e + H_2O, \qquad \text{(II-55)}$$

and from the measurements carried out the recombination coefficient for the inverse process

$$Na^+ + e + H_2O \rightarrow Na + H_2O \qquad \text{(II-56)}$$

may be deduced. The values obtained are almost the same as those for the other species of ion mentioned in the two preceding paragraphs. Indeed Kelly and Padley (1969) comment that there is no detectable dependence of the recombination coefficient on any physical property peculiar to each element (such as the ionization potential or the electronic structure). The comment is not in accord with the expectation that the recombination coefficient should lie closer to the lower than to the upper limit (see Table II-11) if the energy levels of system X are almost hydrogenic. This does not necessarily mean that the physical picture presented here is incorrect; it may merely mean that the semi-quantal method underestimates the recombination coefficient for a hydrogenic system by a factor of about 2 which in theory would not be surprising.

Further measurements are needed, especially on recombination in different gas mixtures.

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III. THE SCATTERING OF THERMAL ELECTRONS BY CARBON MONOXIDE

by A. Dalgarno

ABSTRACT

Close-coupling calculations are carried out for the scattering of electrons with energies up to 0.1 eV by a rigid rotator with dipole and quadrupole moments equal to those of carbon monoxide. By appropriate choice of the short range potential, the experimental data on CO momentum transfer cross sections can be closely reproduced. For the scattering of thermal electrons, CO is similar to N_2 with the addition of a permanent dipole moment. The observed cross section minimum occurs through the addition of the decreasing electron-dipole contribution and an increasing spherically symmetric short range contribution.

Detailed angular distributions are presented for elastic and rotational excitation collisions. Transitions in which the rotational quantum number changes by unity are strongly peaked in the forward direction and transitions in which the rotational quantum number changes by two are nearly isotropic. The elastic scattering is peaked in the backward direction.

A. INTRODUCTION

The cross section for inelastic scattering of low energy electrons in polar gases resulting in excitation of rotational modes of the polar gas is large, for polar molecules with sufficient static dipole moment. Knowledge of the cross section is required in order to study the energy loss process of atmospheric electrons, and in order to determine the rotational temperature of the atmospheric polar molecules. Explicit calculations have been carried out for low energy electrons in CO. Momentum transfer and rotational excitation cross sections have been obtained, including angular differential cross sections.

B. BACKGROUND

There has been much discussion of the scattering of thermal electrons by polar molecules (see Christophorou and Christodoulides 1969, Christo-

phorou and Pittman 1970). A case of particular interest is that of carbon monoxide because swarm data are available that have yielded scattering cross sections over a considerable range of electron energies (Hake and Phelps 1967). An accurate theoretical description is afforded by the close-coupling formalism of Arthurs and Dalgarno (1960), previous calculations of the momentum transfer and rotational excitation cross sections for thermal electrons in CO having been restricted to the first Born approximation (Singh 1970). Close coupling calculations for simultaneous rotational and vibrational excitation at energies above 0.4 eV have been reported (Itakawa and Takayanagi 1969).

C. THEORY

We assume that for the scattering of thermal electrons the molecule can be regarded as a rigid rotator specified by rotational and projection quantum numbers j and m_j. In the close-coupling formalism the angular momentum j of the rotator is compounded with the orbital angular momentum l of the electron to form a total angular momentum J. The interaction potential V(r), where r is the position vector of the electron measured from the centre of mass of the rotator (see Figure III-1), has matrix elements $\langle j'l'; J|V|j''l''; J\rangle$, diagonal in J. between the different channel angular momentum eigenfunctions.

The scattering matrix $S^J(jl;j'l')$ is defined by the requirement that the solution $u^{J,j,l}_{j',l'}(r)$ of the set of coupled equations

$$\frac{\hbar^2}{2\mu}\left[-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}-k^2_{j',l'}\right]u^{J,j,l}_{j',l'}(r) + \sum_{j''}\sum_{l''} \langle j'l'; J|V|j''l''; J\rangle u^{J,j,l}_{j'',l''}(r) = 0 \qquad \text{(III-1)}$$

where $k_{j',l'}$ is the channel wave number, behaves asymptotically as

$$u^{J,j,l}_{j',l'}(r) \sim \delta_{j,j'}\delta_{ll'}\exp\{-i(k_{j,}r-\tfrac{1}{2}l\pi)\} - \left(\frac{k_{l,j}}{k_{j',l'}}\right)^{1/2} S^J(jl;j'l')\exp\{+i(k_{j,}r-\tfrac{1}{2}l\pi)\}$$

(Arthurs and Dalgarno 1960).

Then the differential cross section for scattering through an angle θ with excitation from level j to level j′ is

$$\frac{d\sigma(j\to j';\theta)}{d\theta} = \frac{(-1)^{j'-j}}{4(2j+1)k_{jj}^2}\sum_{\lambda=0}^{\infty} A_\lambda(j\to j')P_\lambda(\cos\theta) \qquad \text{(III-2)}$$

where P_λ are Legendre polynomials and A_λ are expressible in terms of the scattering T matrices

$$T^J(jl;j'l') = \delta_{jj'}\delta_{ll'} - S^J(jl;j'l').$$

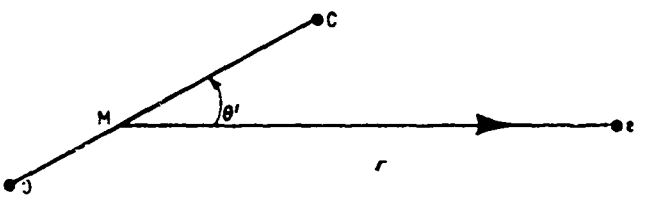

Figure III-1. The coordinates r and θ' are shown. M is the centre of mass of CO.

Introduce the algebraic coefficient

$$Z(abcd;ef) = (-1)^{\frac{1}{2}(f-a+c)}(-1)^{(b+d)}$$
$$\{(2a+1)(2b+1)(2c+1)(2d+1)(2f+1)\}^{1/2}\begin{pmatrix} a & c & f\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} a & b & e\\ d & c & f\end{Bmatrix}$$

where $\begin{pmatrix} a & c & f\\ 0 & 0 & 0\end{pmatrix}$ and $\begin{Bmatrix} a & b & e\\ d & c & f\end{Bmatrix}$ are respectively 3-j and 6-j coefficients. Then

$$A(j\to j') = \sum_{J_1=0}^{\infty}\sum_{J_2=0}^{\infty}\sum_{l_1=|J_1-j|}^{J_1+j}\sum_{l_2=|J_2-j'|}^{J_2+j'}\sum_{l_1'=|J_1-j'|}^{J_1+j'}\sum_{l_2'=|J_2-j'|}^{J_2+j'} \times Z(l_1J_1l_2J_2;j\lambda)Z(l_1'J_1l_2'J_2;j'\lambda) \times T^{J_1}(j'l_1';jl_1)^*T^{J_2}(j'l_2';jl_2). \qquad \text{(III-3)}$$

The total cross section for the $j\to j'$ transition is given by

$$\sigma(j\to j') = \frac{\pi(-1)^{j'-j}}{(2j+1)k_{jj'}^2} A_0(j\to j')$$

$$= \frac{\pi}{(2j+1)k_{jj'}^2} \sum_{J=0}^{\infty} \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} (2J+1)|T^J(jl;j'l')|^2$$

and the momentum transfer cross section is given by

$$\sigma_m(j) = \sum_{j'} \sigma_m(j\to j') = \int \sum_{j'} \frac{d\sigma(j\to j'|\hat{r})}{d\hat{r}} (1-\cos\theta)\, d\hat{r}$$

$$= \frac{\pi(-1)^{j'-j}}{(2j+1)k_{jj'}^2} \sum_{j'} \{A_0(j\to j') - \tfrac{1}{3}A_1(j\to j')\}.$$

D. INTERACTION POTENTIAL

To construct an interaction potential, we assumed initially that apart from its permanent electric dipole of moment 0.112×10^{-18} esu cm, carbon monoxide is essentially similar to the isoelectronic nitrogen molecule (Hake and Phelps 1967). The interaction potential can be written as a sum of a polarization interaction $V_p(r)$, a dipole interaction $V_d(r)$ and a quadrupole interaction $V_q(r)$. For $V_p(r)$ we adopted the form

$$V_p(r) = -\frac{\alpha_0 e^2}{2(r^2+r_0^2)^2} \qquad r \leqslant r_p$$

$$= -\frac{\alpha_0 e^2}{2(r^2+r_0^2)^2} - \frac{\alpha_2 e^2}{2(r^2+r_0^2)^2} \frac{(r-r_p)^2}{b_p^2+(r-r_p)^2} P_2(\cos\theta') \qquad r \geqslant r_p$$

where $\alpha_0 = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)$ $\qquad \alpha_2 = \frac{2}{3}(\alpha_\parallel - \alpha_\perp)$

$\alpha_\parallel$ and $\alpha_\perp$ being respectively the parallel and perpendicular polarizabilities (see Hirschfelder et al. 1954), and r_0, r_p and b_p are disposable parameters. The argument r is the position vector of the electron relative to the center of mass of CO, and θ' is the angle between r and the molecular axis. For $V_q(r)$ we adopted the form

$$V_d(r) = 0 \qquad r \leq r_d$$
$$V_d(r) = \frac{eD}{r^2}\frac{(r-r_d)^2}{b_d^2+(r-r_d)^2}P_1(\cos\theta') \qquad r \geq r_d$$

where D is the dipole moment of carbon monoxide, and for $V_q(r)$ the form

$$V_q(r) = 0 \qquad r \leq r_q$$
$$V_q(r) = \frac{eQ}{r^3}\frac{(r-r_q)^2}{b_q^2+(r-r_q)^2}P_2(\cos\theta') \qquad r \geq r_q$$

where Q is the quadrupole moment of carbon monoxide (the Q_{zz} of Stogryn and Stogryn 1966), and r_d, b_d, r_q and b_q are disposale parameters.

The potentials V_p, V_d and V_q have the correct asymptotic behaviors

$$V_p(r) \sim -\tfrac{1}{2}\frac{\alpha_0 e^2}{r^4} - \tfrac{1}{2}\frac{\alpha_2 e^2}{r^4}P_2(\cos\theta')$$
$$V_d(r) \sim \frac{eD}{r^2}P_1(\cos\theta')$$
$$V_q(r) \sim \frac{eQ}{r^3}P_2(\cos\theta').$$

The form of the spherically symmetric part of $V_p(r)$ is that which proved successful in the interpretation of the scattering of low energy electrons by molecular nitrogen (Sampson and Mjolsness 1965) and its short range behavior reflects in a phenomenological way the effect of exchange forces. The elastic scattering cross sections depend initially on the short range spherically symmetric component of $V(r)$ and we chose r_0 so that our calculations reproduced the momentum transfer cross section measured at the energy of 0.03 eV.

The interaction of an electron with carbon monoxide cannot be properly described by a local velocity independent potential for values of r smaller than the equilibrium C-O separation for r_e. The cross sections for thermal electrons are however, insensitive to the detailed form of the orientation-dependent terms for $r \leq r_e$ and we imposed arbitrarily the requirements that V_d and V_q vanish for $r \leq \frac{1}{2}r_e$ and $r \leq \frac{3}{4}r_e$ respectively, these values being our estimates of where the corresponding components of the static field of CO change sign. We terminated the angular term in V_p also at $r = \frac{1}{2}r_e$.

The values adopted for the potential parameters are listed in Table III-1. The dipole polarizabilities are taken from Bridge and Buckingham (1966), the dipole moment from Barnes (1958) and the quadrupole moment from Stogryn and Stogryn (1966).

E. CALCULATIONS

Because of the long range of the electron-dipole interaction, many partial waves contribute to the scattering. Even close to threshold, over 100 values of J must be retained. The computational difficulty can be avoided by recognizing that as J increases, the exact T matrices rapidly approach the first Born approximation T matrices. Indeed in no

TABLE III-1. **Values of the potential parameters in $V(r)$**

Parameter	Value
α_0	1·977 Å^3
α_2	0·355 Å^3
r_0	0·693 Å
r_p	0·564 Å
b_p	0·1 Å
D	$0{\cdot}112 \times 10^{-18}$ esu cm
r_q	0·564 Å
b_q	0·1 Å
Q	$-2{\cdot}5 \times 10^{-26}$ esu cm^2
r_q	0·846 Å
b_q	0·1 Å

case did we find it necessary to solve the close-coupled equations (III-1) for $J > 7$. The T^J matrices for the first Born approximation, T_B^J, can be easily calculated. With the long range electron-dipole interaction, the first Born approximation allows only transitions in which j changes by unity, and with the long range electron-quadrupole interaction, the first Born approximation allows only transitions in which j changes by two (for Σ states of diatomic molecules). For both interactions, the first Born differential scattering cross sections take simple forms (see Crawford et al. 1967).

The direct evaluation of the summations (III-2) and (III-3) is tedious. Equation (III-3) has the structure

$$A_\lambda = \{T^{0\dagger}, T^{1\dagger}, \ldots T^{\infty\dagger}\} X_\lambda \begin{bmatrix} T^0 \\ T^1 \\ \vdots \\ T^\infty \end{bmatrix}$$

where T^J is a column vector whose elements comprise all the T matrix elements with angular momentum J, $T^{J\dagger}$ is a row vector that is the Hermitian conjugate of T^J and X_λ is a symmetric matrix. When T^J is replaced by the Born matrices T_B^J for J greater than or equal to some value F, A_λ becomes

$$A_\lambda'(F) = \{T^{0\dagger}, \ldots T^{F-1\dagger}, T_B{}^{F\dagger}, \ldots T_B{}^{\infty\dagger}\} X_\lambda \begin{bmatrix} T^0 \\ \vdots \\ T^{F-1} \\ T_B{}^F \\ \vdots \\ T_B{}^\infty \end{bmatrix}. \qquad \text{(III-4)}$$

The Born approximation itself is $A_\lambda'(0)$. The matrix X_λ connects only those elements T^J and $T^{J'}$ such that $|J-J'| \leq \lambda$. Thus

$$A_\lambda'(F) - A_\lambda'(0) = \{T^{0\dagger}, \ldots T^{F-1\dagger}, T_B{}^{F\dagger}, \ldots T_B{}^{F+\lambda\dagger}\} X_\lambda \begin{bmatrix} T^0 \\ \vdots \\ T^{F-1} \\ T_B{}^F \\ \vdots \\ T_B{}^{F+\lambda} \end{bmatrix}$$

$$- \{T_B{}^{0\dagger}, \ldots T_B{}^{F+\lambda\dagger}\} X_\lambda \begin{bmatrix} T_B{}^0 \\ \vdots \\ T_B{}^{F+\lambda} \end{bmatrix}.$$

$A_\lambda'(0)$ can be calculated from the analytical form of the Born approximation differential scattering cross section (see Crawford et al. 1967) and the direct evaluation of an infinite sum, as in (III-4), is avoided.

The values of A_λ for large values of λ are needed only for the construction of the differential scattering cross section at small angles. But for large values of λ, A_λ and A_λ' approach the Born approximation $A_\lambda'(0)$. Thus if ℓ and F are sufficiently large,

$$\frac{d\sigma}{d\hat{r}}(j\to j'|\hat{r}) = \frac{d\sigma_B(j-j'|\hat{r})}{d\hat{r}} + \frac{(-1)^{j'-j}}{4(2j+1)k_{jj}^2}\sum_{\lambda=0}^{l}(A_\lambda'(F)-A_\lambda'(0))P_\lambda(\cos\theta)$$

where $d\sigma_B/d\hat{r}$ is the Born approximation to the differential scattering cross section.

F. RESULTS

It is clear from the comparison of the first Born approximation and the fixed rotator approximation of Altshuler (1957) that, except very close to the excitation thresholds, the momentum transfer cross section for electrons scattered by CO is nearly independent of the initial rotational state of CO (Crawford et al. 1967, Bottcher 1970, Crawford 1970) and accordingly of the gas temperature. Thus the close-coupling results, obtained from the numerical integration of (III-1), yielded a value of 7.41 $\mathring{A}^2$ for σ_m at 0.1 eV both for an initial j of 0 and of 10. At 5×10^{-3} eV, the values of σ_m for j = 0 and j = 3 were respectively 13.5$\mathring{A}^2$ and 13.0 $\mathring{A}^2$. The remainder of our calculations were carried out with j = 0.

The value of r_0 that reproduces the experimental cross section at 0.03 eV is 0.693$\mathring{A}$. Figure III-2 compares the close-coupling results for σ_m with the measured values at other energies and demonstrates that the harmony between theory and measurement is maintained. Figure III-2 also includes the Altshuler approximation (1957), which is essentially equivalent to the first Born approxkmation corresponding to the electron-dipole interaction (Crawford et al. 1967). At low energies the collision is dominated by rotational transitions due to the electron-dipole interaction and because the scattering is strongly peaked in the forward direction and the dipole moment is not large, the scattering is accurately described by the first Born apprcximation. The cross section due to the electron-

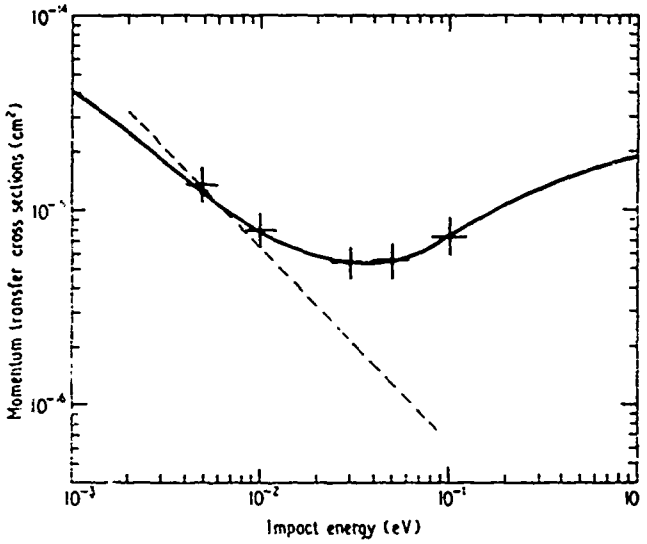

Figure III-2. The momentum transfer cross section for electrons in CO. Full curve derived from swarm data by Hake and Phelps (1967); broken curve, the Born approximation of Altshuler (1957); ×, the results of our close-coupling calculations.

dipole interaction decreases as E^{-1}. The observed minimum in σ_m near 0.03 eV occurs because at higher energies, the elastic scattering by the spherical component of V(r) provides the dominant contribution to σ_m. The contribution from quadrupole excitation to $j' = 2$ levels is nearly independent of energy and it is not negligible. Thus scattering by CO is qualitatively similar to scattering by N_2 with the addition of electron-dipole scattering. A detailed analysis is given in Table III-2 which lists the individual contributions to σ_m from elastic scattering $\Delta j = j'-j = 0$,

TABLE III-2. Momentum transfer cross sections in Å²

Energy (eV)	0·005	0·01	0·03	0·05	0·1
$\sigma_m(0 \to 0)$	0·51	0·97	2·39	3·51	5·75
$\sigma_m(0 \to 1)$	11·83	5·86	1·90	1·12	0·55
$\sigma_m(0 \to 2)$	0·96	1·03	1·06	1·07	1·10
$\sigma_m(0)$	13·30	7·86	5·35	5·70	7·40

single quantum excitation $\Delta j = 1$ and two quantum excitation $\Delta j = 2$. There occur some contributions to $\Delta j = 0$ and $\Delta j = 2$ transitions from the virtual

dipole-dipole sequences but for CO they are not large and almost all of $\sigma_m(0 \to 0)$ arises from $V_p(\hat{r})$ and almost all of $\sigma_m(0 \to 2)$ from $V_q(r)$. For scattering by a molecule with a large dipole moment such as CN (Itikawa and Takayanagi 1969, Crawford, Allison and Dalgarno 1969), the situation is reversed.

The elastic and excitation cross sections $\sigma(0 \to j')$ are listed in Table III-3. The values of $\sigma(0 \to 1)$ are close to those given by the first Born approximation.

TABLE III-3. **Total elastic and excitation cross sections in Å²**

Energy (eV)	0·005	0·01	0·03	0·05	0·1
$\sigma(0 \to 0)$	0·40	0·74	1·78	2·58	4·15
$\sigma(0 \to 1)$	45·06	26·87	11·20	7·34	4·09
$\sigma(0 \to 2)$	0·96	1·03	1·07	1·08	1·11
$\sigma(0)$	46·42	28·64	14·05	11·00	9·35

The differences between $\sigma(j \to j')$ and $\sigma_m(j \to j')$ are a consequence of the angular distributions $d\sigma(j \to j')/d\hat{r}$. The calculated distributions are illustrated in Figures III-3, III-4 and III-5. Those for $d\sigma(0 \to 1)/d\hat{r}$ are given in the form of the ratio to the distribution, $d\sigma_B/d\hat{r}$, obtained from the first Born approximation for the electron-dipole interaction. The angular distributions are required in the theory of recombination in molecular gases developed by Bates et al. (1970).

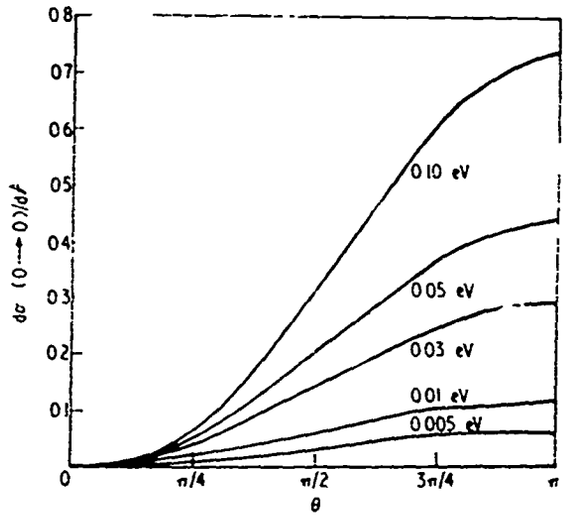

Figure III-3. The angular distribution of electrons of various energies scattered by CO in an elastic $0 \to 0$ rotational transition.

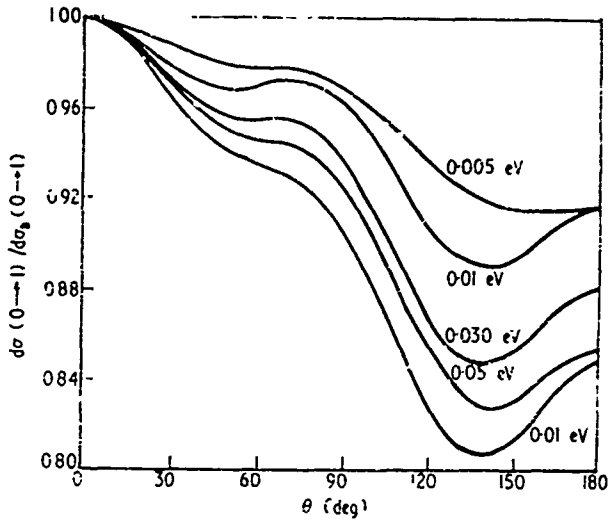

Figure III-4. The angular distribution of electrons of various energies scattered by CO in an inelastic 0→1 rotational transition. The distribution is given as the ratio to the angular distribution calculated from the Born approximation assuming an electron-dipole interaction.

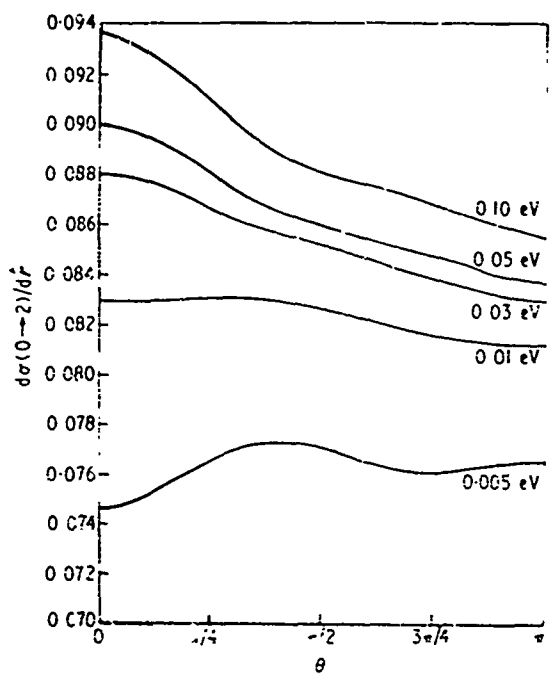

Figure III-5. The angular distribution of electrons of various energies scattered by CO in an inelastic 0→2 rotational transition.

The differential cross section for $\Delta j = 1$ scattering is charply peaked at small angles behaving there almost as $(1-k_{jj'}\cos\theta/k_{jj})^{-1}$, as expected for an electron-dipole interaction (see Takayanagi 1966, Crawford et al. 1967), and the differential cross section for $\Delta j = 2$ scattering is nearly isotropic as expected for an electron-quadrupole interaction (Gerjuoy and Stein 1955). The elastic scattering cross section depends upon the detailed form of V(r) and with our choice it peaks in the backward direction. The $(1-\cos\theta)$ factor in σ_m suppresses the strong forward peak associated with $\Delta j = 1$ scattering and $\sigma_m(0\rightarrow 1)$ is much smaller than $\sigma(0 \rightarrow 1)$. The cross sections are comparable both for $\Delta j = 0$ and $\Delta j = 2$ transitions.

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IV. ASSOCIATIVE DETACHMENT OF O AND O^-

by A. Dalgarno and J. C. Browne

Theoretical studies of the rate coefficient for the associative detachment reaction

$$X + Y^- \rightarrow XY + e$$

requires accurate knowledge of the potential energy curves for both the neutral and negative ion molecule. Also required are calculations of the half-width for the radiationless transition. The calculation of the half-width is very difficult for complex systems, so that entirely predictive calculations have been carried out only for the simple reaction (Ref. I-3)

$$H + H^- \rightarrow H_2 + e$$

A critical parameter in the calculation of the rate coefficient for associative detachment of O and O^-:

$$O + O^- \rightarrow O_2 + e$$

are the interaction energies at the intersections of the O_2^- and O_2 potential energy curves. If any one of the crossing points lies energetically below the asymptotic limit at infinite separation , the process can be expected to be rapid at thermal velocities.

Accordingly we have carried out elaborate configuration interaction calculations for the $^2\Pi_g$ and $^2\Pi_u$ status of O_2^- as an extension of our previous work.

The orbital exponents for the 2p orbitals were chosen so that the resulting curve had an electron affinity of 0.43 eV with respect to the Schaefer-Harris calculations for O_2 (J. Chem. Phys. 48, 4946, 1968), when it is adjusted so that the difference of the separated atom limit and

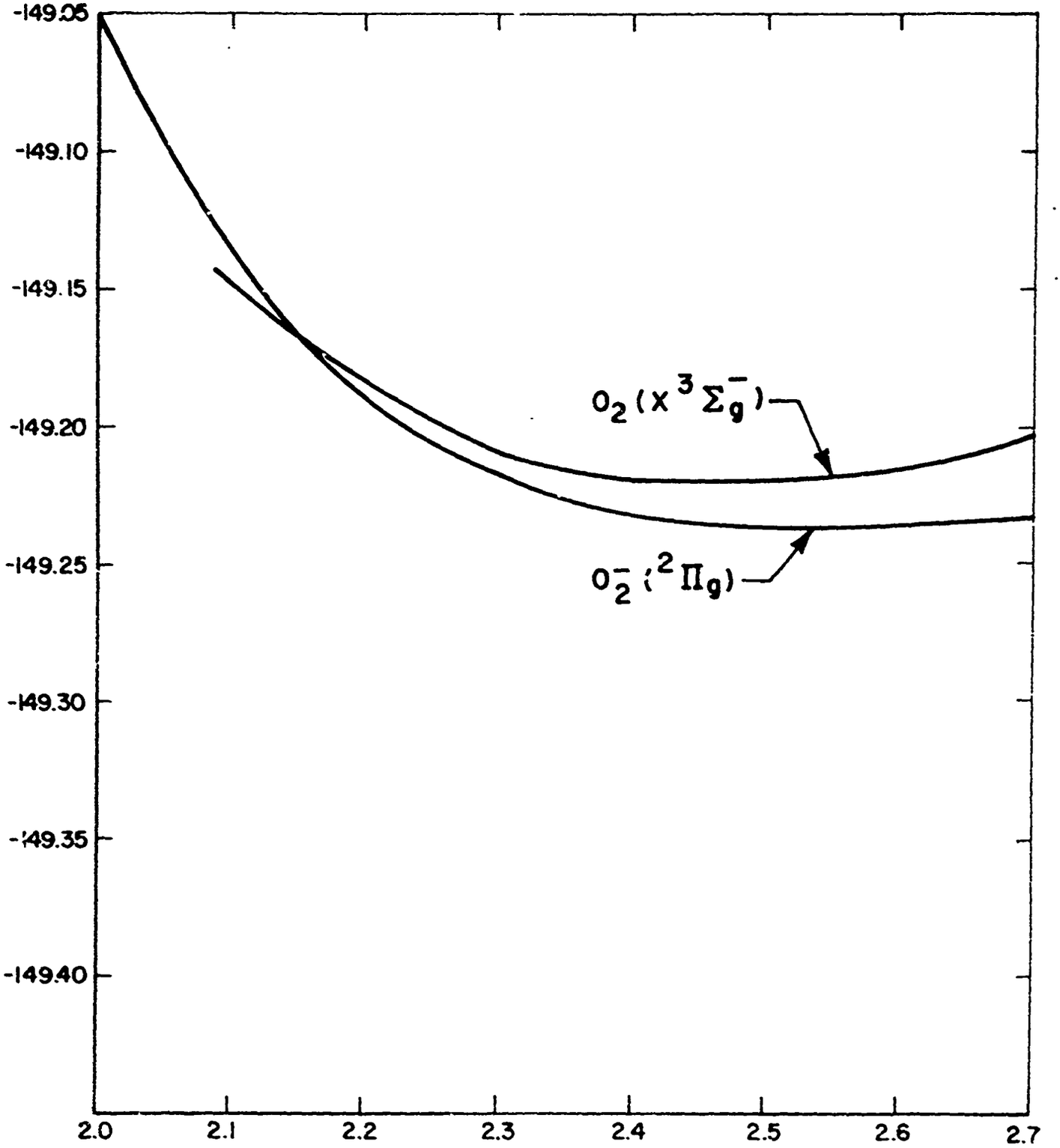

Figure IV-1. Potential energy curves of $O_2(X^3\Sigma_g^-)$ and $O_2^-(^2\Pi_g)$

the Schaefer-Harris O_2 curve has the experimental value. The $O_2^-(^2\Pi_g)$ crosses the $O_2(X\ ^3\Sigma_g^-)$ curve at a separation of about 2.15 a_o at an energy <u>below</u> the asymptotic limit. The precise value of the crossing is uncertain because we have discovered shift errors in the published Shaefer-Harris O_2 curves that will have to be corrected. However, there seems to be no doubt that approach along the $^2\Pi_g$ curve leads to associative detachment at thermal velocities.

V. PSEUDO-POTENTIAL CALCULATION OF ATOMIC INTERACTIONS

by A. Dalgarno and G. A. Victor

ABSTRACT

The use of atomic psuedo-potentials in calculations of atomic interactions is briefly discussed. It is shown that an appropriate choice of pseudo-potential leads to the appearance of the van der Waals interactions in first order. Care is needed in the choice of the core-core interaction potential lest spurious long-range forces appear. Explicit calculations are reported for the $^2\Sigma_g^+$ and $^2\Sigma_u^+$ ground states of Li_2^+ and comparison made with the results of conventional calculations. High accuracy is obtained over a wide range of internuclear separations.

A. INTRODUCTION

Rydberg-Kelin-Rees (RKR) methods yield accurate potential energy curves for diatomic molecules for spectroscopically measured attractive potential curves in the neighborhood of the equilibrium internuclear separation. Similarly, at very large internuclear separations, ab-initio or semi-empirical methods lead to detailed knowledge of the van der Waals terms for various molecules. For intermediate internuclear separations, much less data are available. Semi-empirical, effective potential methods can provide accurate data for selected systems at intermediate internuclear separations, where other methods are inappropriate. For many processes of atmospheric interest, such data are a prerequisite for quantitative predictions. Preliminary studies of the molecular potential curves for Li_2^+ have been carried out using accurate semi-empirical effective potential techniques. The results are very encouraging, as the current results compare very favorably with very elaborate ab-initio calculations. Such procedures can be, in principle, extended to more complex systems as long as the number of essential valance electrons is not large. A review of these studies is given in the following discussions. Further preliminary calculations, for alkali systems on inert gases have been carried out which demonstrate the utility of the methods

for scattering problems. Using these methods, limited to one valance electron, studies can be made of charge transfer processes in alkali-alkali ion systems as well as quenching processes in alkali-inert gas systems. Treatment of up to two valance electrons is very possible, leading to the possibility of studying many diverse atomic scattering problems; however, it seems that relevant data for few processes of interest for normal and disturbed atmospheres can be obtained without encountering severe difficulties.

B. DETAILED DISCUSSION

Psuedo-potential or model potential methods have been successfully applied to several problems of quantum chemistry (Ref. V-1) and they can also be of value in the determination of interatomic forces at intermediate and large nuclear separations. Consider a Rydberg electron with quantum numbers $n\ell$ and position vector r_a moving in the field of a spherical core with excess charge Z_a located at the origin A of coordinates and construct an effective single channel potential $V_a(r_a)$ with eigenvalues equal in magnitude to the observed ionization potentials $E_a(nl)$ of the Rydberg states. Suppose that this atomic system is interacting with another spherical core B at a distance R from A and that the binding energies of the valance states associated with the second core can be reproduced by an effective potential $V_b(r_b)$. The problem of calculating the adiabatic interatomic potential $\epsilon(R)$ reduces to finding the appropriate solution of the one-electron equation (written in atomic units)

$$\{-\tfrac{1}{2}\nabla^2 + V_a(r_a) + V_b(r_b) + V_C(R, r_a, r_b) - \epsilon(R)\}\ \Psi(r_a) = 0\,, \qquad \text{(V-1)}$$

where V_C represents the effects of the core-core interaction. At large distances R, the system dissociates to a Rydberg state of either A or B.

Suppose we are interested in the state that dissociates into the $n\ell$ state of A with wavefunction $\phi_a(nl\ r_a)$. such that

$$\{-\tfrac{1}{2}\nabla^2 + V_a(r_a) - E_a(nl)\}\ \phi_a(nl) = 0\ . \qquad \text{(V-2)}$$

then at large distances R , to first order,

$$\epsilon(R) = \langle \phi_a(nl|r_a)|V_b(r_b) + V_C(R, r_a, r_b)|\ \phi_a(nl|r_a)\rangle\ . \qquad \text{(V-3)}$$

If we include a polarization term in the core potential, then asymptotically

$$V_b(r_b) \simeq -\frac{Z_b}{r_b} - \frac{\alpha_b}{2r_b^4}\ , \qquad \text{(V-4)}$$

where α_b is the dipole polarizability of the core. Hence for spherically symmetric systems,

$$\epsilon(R) \simeq \langle ns|V_C(R, r_a, r_b)|ns\rangle - \frac{Z_b}{R} - \frac{\alpha_b}{2R^4} - \frac{\alpha_b}{R^6}\langle ns|r_a^2|ns\rangle\ . \qquad \text{(V-5)}$$

It is clear that the core-core potential $V_C(R, r_a, r_b)$ must contain asymptotically not only the nuclear term $Z_a Z_b / R$ but also the polarization term $(-\tfrac{1}{2})\alpha_b R^4$. The omission of the polarization term would be particularly serious for a neutral core with $Z_b = 0$. A plausible choice for $V_C(R, r_a, r_b)$ is

$$(Z_a - 1)\frac{Z_a Z_b}{R} + (Z_a - 1)^2\,[V_b(R) - V_b(R)]\ . \qquad \text{(V-6)}$$

if the molecular system idssociates to a Rydberg state of A.

The R^{-6} term in $\epsilon(R)$ is the van der Waals interaction. It here appears in first order, rather than in second order as in conventional approaches, and it is easily reproduced by variational solutions of the one-electron eigenvalue equation for $\epsilon(R)$. The van der Waals interaction can be written in the firm

$$C = -\frac{3}{2R^6} \sum_m \sum_n \frac{f^a_m f^b_n}{(\epsilon^a_0 - \epsilon^a_m)(\epsilon^b_0 - \epsilon^b_n)(\epsilon^a_0 + \epsilon^b_0 - \epsilon^a_m - \epsilon^b_n)} \quad \text{(V-7)}$$

where the f's are oscillator strengths and the ϵ's are atomic eigenvalues. If we assume that the transition energies $(\epsilon^a_0 - \epsilon^a_m)$ of the Rydberg system A are much smaller than those $(\epsilon^b_0 - \epsilon^b_n)$ of the core B, it follows that (Ref. V-2).

$$C = -\alpha_b \langle ns | r_a^2 | ns \rangle R^6 . \quad \text{(V-8)}$$

Our choice of pseudo-potential leads to the same asymptotic interaction. The numerical value given by (V-8) is -3.39, whereas the correct value is -3.32 (Ref. V-3).

Conventional calculations of the interaction energies of Li_2^+ have been reported by Bardsley (Ref. V-4) and they provide a valuable quantitative test of our model. We adopt the representation in atomic units

$$V_{Li^+}(r) = V_{HF}(r) - \frac{0.09615}{r^4}\{1 - \exp[-(r\ 0.47)^6]\} - \frac{0.0073}{r^6}\{1 - \exp[-(r/0.44)^8]\} \quad \text{(V-9)}$$

where $V_{HF}(r)$ is the Hartree-Fock core potential. This potential (V-9) has a 2s eigenvalue of -0.19824 au compared to the experimental value -0.19814 au and a 2p eigenvalue of -0.13039 au compared to the experimental value -0.13024 au. An accurate 2s - ap energy difference is important in ensuring that the interactions have the correct (second-order) asymptotic form -1/2 α/R where α is the dipole polarizability of neutral lithium. The pseudo-potential gives a 2s - 2p energy difference of 0.06785 au compared to the experimental difference 0.06790 au.

We have solved the one-electron eigenvalue equations for $\epsilon(R)$ for the $\sigma_g(2s)$ and $\sigma_u(2s)$ orbitals by standard variational procedures except that the molecular integrals involving the pseudo-potentials were evaluated by numerical quadrature. The results are compared with those of

Bardsley in Figure V-1. The agreement is close over a wide range of separations. For the ground state of Li_2^+ we obtain a dissociation energy of 1.30 eV at our equilibrium separation of 6.0 a_0 whereas Bardsley (1970) obtains 1.22 eV at 5.8 a_0. Asymptotically we find

$$\epsilon(R) \simeq -\frac{80.7}{R^4} - \frac{2926}{R^6} . \qquad \text{(V-10)}$$

The choice of $V_C(R, r_a, r_b)$ is not unique. Indeed of particular importance for $l \neq 0$, a more accurate representation, correct at large R, is provided by

$$V_C(R, r_a, r_b) = \frac{Z_a Z_b}{R} - Z_a V_b(R) - Z_b V_a(R) - \frac{Z_b \alpha_a R \cdot r_a}{R^3 r_a^3} \omega_a(r_a) - \frac{Z_a \alpha_b R \cdot r_b}{R^3 r_b^3} \omega_b(r_b) - \frac{Z_a^2 \alpha_b}{2R^4} - \frac{Z_b^2 \alpha_a}{2R^4} , \qquad \text{(V-11)}$$

where $\omega_a(r)$, $\omega_b(r)$ are suitable cut-off functions. In the case of Li^+ we took

$$\omega(r) = 1 - \exp[-(r\ 0.47)^6] . \qquad \text{(V-12)}$$

as suggested by Equation (V-9). Asymptotically, $\epsilon(R)$ behaves correctly according to

$$\epsilon(R) \simeq \frac{-\alpha_b}{R^6} \langle nl\ r_a^2 [1 + P_2(\cos\theta_a)] | nl \rangle \qquad \text{(V-13)}$$

(see Baylis, Ref. V-5). For $l = 0$ the P_2 term vanishes. We have employed the more complicated form of V_C in a calculation of $\epsilon(R)$ for the $^2\Sigma_g^+$ state at R = 6.0 a_0. The binding energy is changed from 1.30 eV to 1.28 eV.

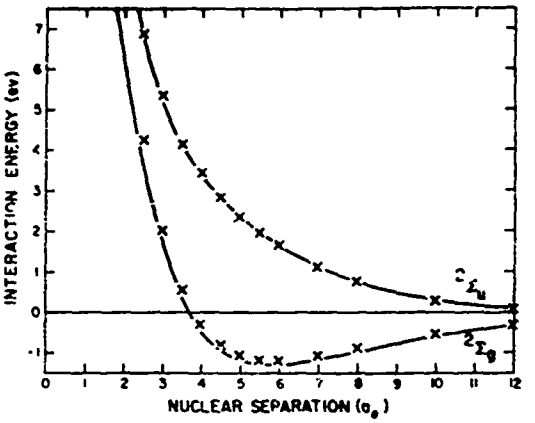

Figure V-1. The interaction energies for the lowest $^2\Sigma_g$ and $^2\Sigma_u$ states of Li_2^+. The full curves are the results of our pseudo-potential calculations. The crosses are the results of the refined variational calculations of Bardsley (Ref. V-4).

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VI. CONCLUSIONS AND RECOMMENDATIONS

Detailed studies of atmospheric behavior following nuclear or natural (aurora or PCE events) disturbances requires accurate data on cross sections and rate coefficients for a highly diverse ensemble of atomic, molecular, chemical, and transport processes. In recent years, experimental studies and in a more modest way, theoretical investigations supported by DNA have provided essential input data for subsequent computer modeling of atmospheric response. Owing to the relatively wide range of possible initial conditions, the complexity of the overall problem, and the inevitable delay between identification of important processes and the subsequent generation of accurate input data, understandable time delays occur between input data,generation data and application to computer coding. As a consequence, data requirements and thus emphasis on specific processes change periodically. Depending on the accuracy requirements imposed on the input data, decisions on whether to employ experimental, theoretical, or a combination of approaches become important from both time and economy criteria. Such decisions are complicated by the fact that equilibrium thermodynamic conditions are seldom encountered, so that detailed cross section data are usually required.

GCA Technology Division has for several years been performing theoretical studies directed towards the satisfaction of these requirements. Emphasis has been directed towards the study of those processes which control the degree of atmospheric ionization, particularly for those processes which are important for recombination. Basic cross sections have been investigated rather than reaction rates, in order to cope with the non-thermal equilibrium requirements of many applications.

A major portion of our investigations has been concerned with the process of three-body ion-electron recombination in dense gases at low temperatures (Section II). In such complex systems, one must resort to semi-quantal, statistical theories, which should lead to results of acceptable accuracy for the necessary applications. The studies per-

formed to date yield sufficient data for useful extensions, without extensive calculation, for predictions for various ions, temperatures, third body concentrations, and third body systems expected to be of importance. Further significant progress leading to increased accuracy can only be obtained by a major reformulation of the theory requiring significant theoretical progress in complex many-body problems. Such progress is unlikely in the near future so that additional extensive theoretical study of the process is not indicated at this time. The body of data generated to date, serves as a useful basis for interpolation and extrapolation for systems not yet studied.

The results presently available for study of the process of associative detachment are preliminary in nature. The calculations for the potential energy curves for $O + O^-$ should be continued in order to provide more accurate data, especially in the region of the important curve crossings. Similar studies should be performed for the $N + O^-$ system. Only an upper limit for the cross section for associative detachment can be obtained from the potential energy curve data. Accurate quantitative predictions require the calculation of certain coupling matrix elements. Two methods can be suggested for the evaluation of these necessary matrix elements. One involves the evaluation of the electronic molecular Hamiltonian for complex energies whereas the other involves the direct evaluation of the coupling matrix elements using single center molecular eigenfunctions. Both methods are within the state-of-the-art for large scale molecular calculations, and should be investigated in greater detail for possible application to the problem of associative detachment.

The studies of the use of effective potential methods for atomic and molecular processes has provided highly accurate results. However, in the present form, they are of limited use for important atmospheric species and progresses, so that more extensive studies are not indicated for future progress.

Two areas of study should be introduced into future programs. The first involves the use of classical and semi-quantal methods for the

theoretical investigation of several classes of ion-molecule reactions. This study is indicated at the present time because the classical and semi-quantal methods appear to yield accurate results for many processes, and ion-molecule reactions form an important class of reactions in the overall understanding of disturbed atmospheres.

Higher energy processes are becoming of increased importance in disturbed atmosphere studies. Because of recent theoretical progress, quantitative studies of the process of diaelectronic recombination are becoming possible. As a consequence, a renewed study of diaelectronic recombination should be initiated.

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13 ABSTRACT

This report presents the findings of a number of individual investigations relevant to the physics of atomic and molecular processes in the upper atmosphere as pertinent to the problem of the rate of reduction of ionization in a disturbed atmosphere.

Calculations have been performed of the rates for three-body ion-electron recombination

$$X^+ + e + M \rightarrow X + M$$

for a variety of ions X^+ and third bodies M. Emphasis has been placed on systems where the third body involves a molecular species. It has been shown that if the third body has low energy modes of internal excitation, large recombination rates may result. If M is a polar mole-

(Continued on page 79)

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cule, very large recombination rates will result. The calculations show that the rate for three-body ion-electron recombination is very sensitive to the concentration of water vapor.

The process of associative detachment

$$X^- + Y \rightarrow XY + e$$

is an important mechanism for the removal of negative atomic and molecular ions. Only sparse accurate experimental data exist, and quantitative theoretical data exist only for H^- + H collisions. Quantitative prediction of the rate coefficient for associative detachment requires accurate potential energy curves for the negative molecular ion XY^- and the neutral molecule XY, especially in any regions of curve crossings involving the lower levels of the molecules. Also required are certain non-radiative coupling matrix elements between the electronic states of the molecules. The theoretical calculation of the necessary accurate potential energy curves and matrix elements represents a relatively difficult theoretical problem for species of interest in the atmosphere. From knowledge of the potential energy curves, useful upper limits for the rate of associative detachment can be obtained. Improved calculations of potential energy curves O_2^-, relative to theoretical O_2 curves, have been performed for the important atmospheric process

$$O^- + O \rightarrow O_2 + e$$

the cross section could be as large as $4.6\ \pi a_o^2$.

The cross section for rotational excitation in electron polar molecule collisions,

$$e + M(J) \rightarrow e + M\ (J + \Delta J),$$

where M(J) is a polar molecule in rotational state J, is large. Rotational excitation processes represent an important energy loss mechanism for the thermalization of supra-thermal electrons produced by an atmo-

spheric disturbance. Since most recombination processes proceed much more rapidly for low energy electrons than for supra-thermal electrons, the rotational excitation process plays an important role in the rate of reduction of ionization in a disturbed atmosphere. The cross section for this process constitutes an essential input data point for the studies of three-body ion-electron recombination in polar gases. Detailed calculations have been performed for the cross section for rotational excitation of carbon monoxide by electron impact using close-coupling methods.